Journal of CHEMICAL EDUCATION

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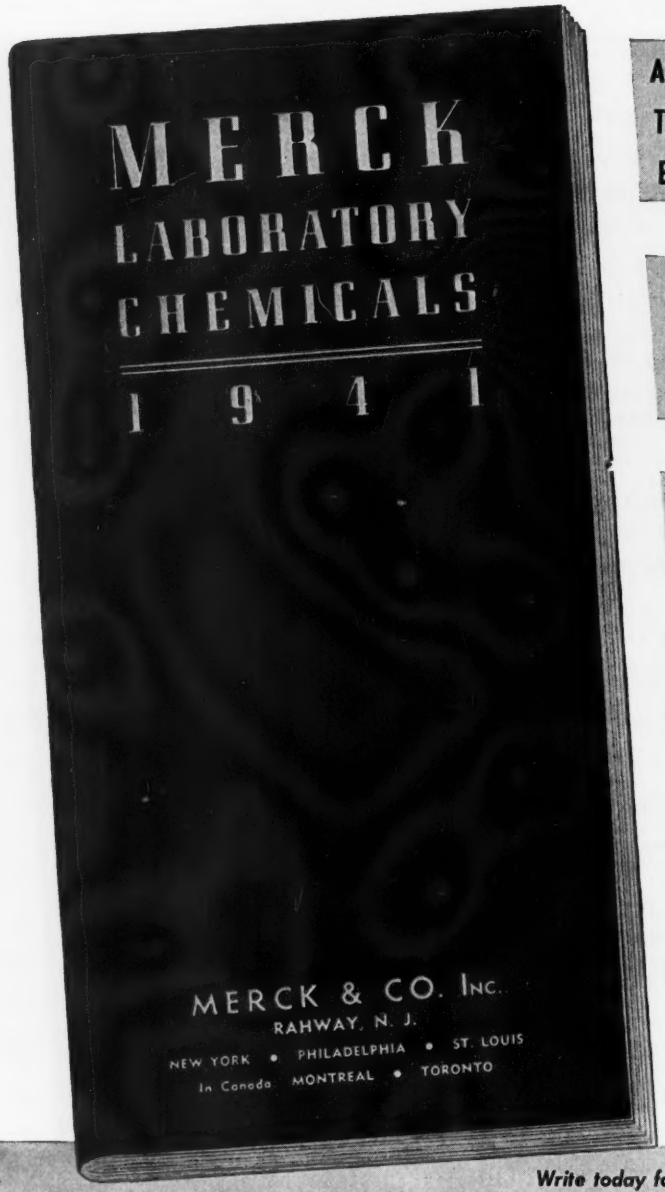

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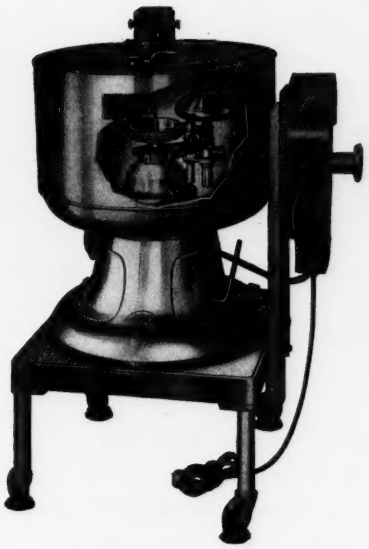

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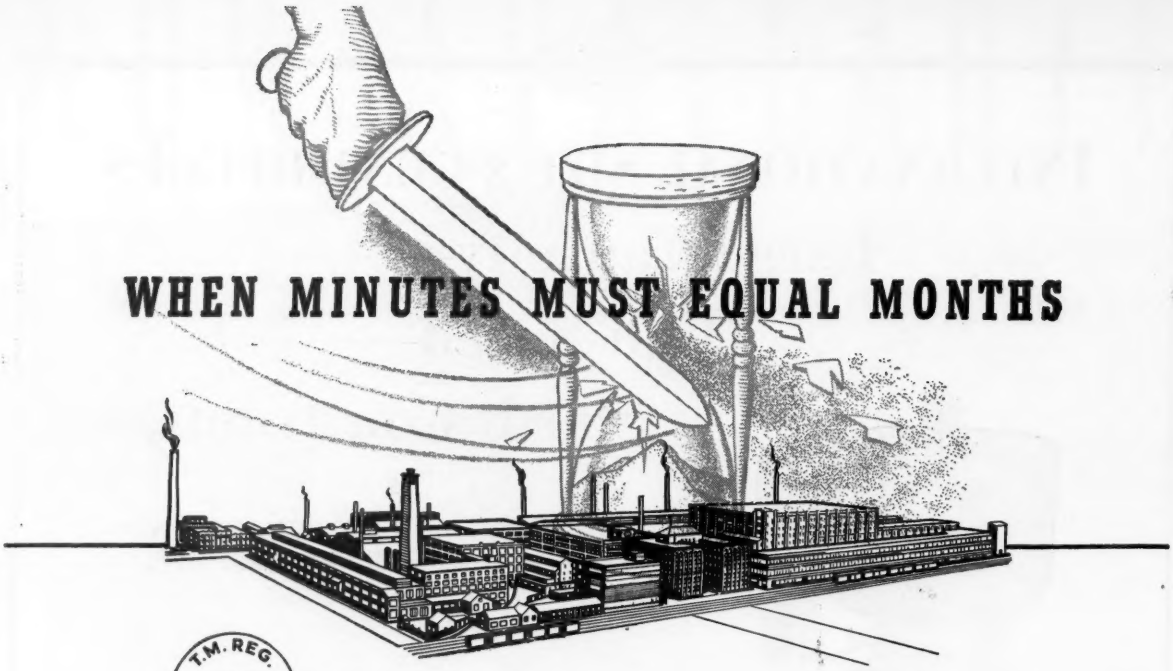

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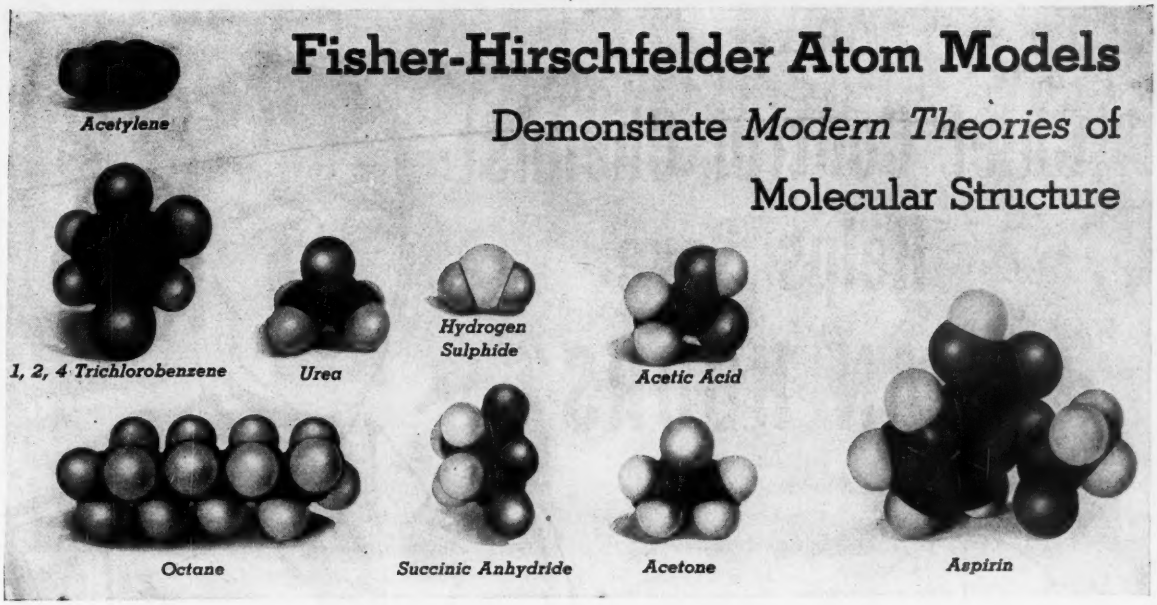

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6	1.05	270	12.00	25	1.45	41	7.20
7	1.10	218	10.20	28	1.15	45	9.60
8	1.10	188	10.20	30	1.25	37	9.60
9	1.15	158	9.00	32	1.35	34	9.60
10	1.15	139	9.00	35	1.35	30	9.60
11	1.20	120	9.00	38	1.40	26	11.40
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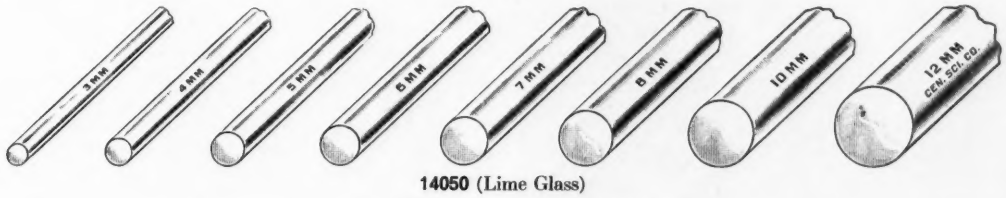

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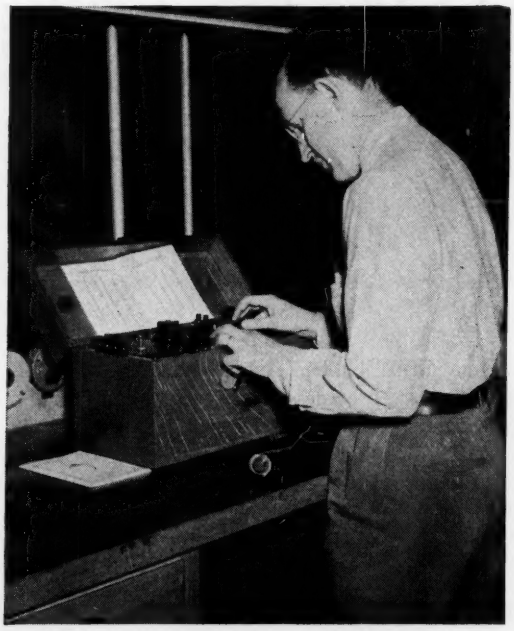

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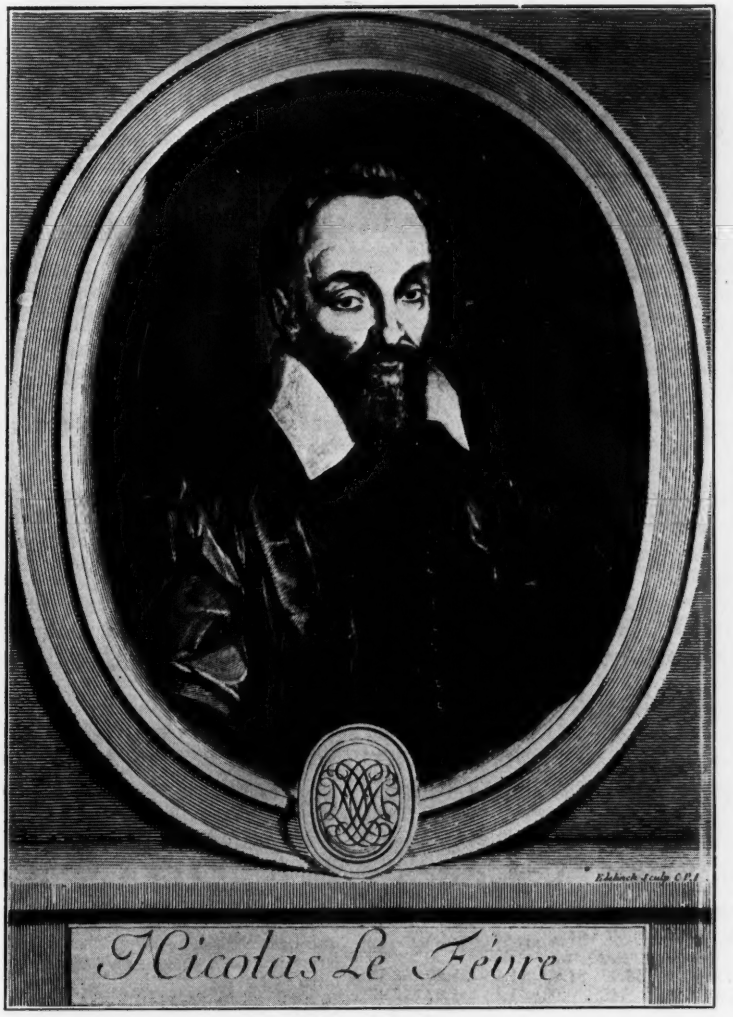

Nicolas Le Fevre
(1600–69)

(For further information see the article, "Early Chemistry at Le Jardin du Roi," by Clara de Milt, on page 503.)

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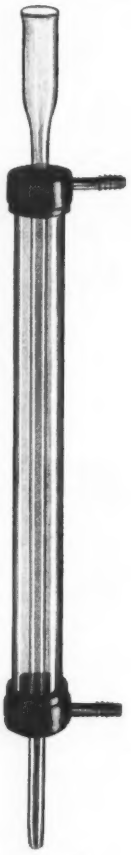

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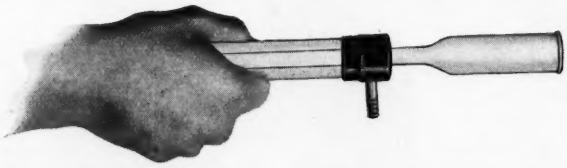

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Lots of 36, Ea.	.27	.31	.40	.45	.67	1.12	1.80

4943. INNER TUBE, ONLY, For Straight-Jacket Condenser.

For Condenser. Length, mm.	250	300	400	500	600	750	900
Inner Tube Length, mm.	500	550	650	750	850	1000	1150
Each.....	$0.27	$0.30	$0.32	$0.34	$0.38	$0.40	$0.65
Lots of 36, Ea.	.25	.27	.29	.31	.35	.36	.58

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4941P. CONDENSER, STRAIGHT-JACKET, Pyrex. This is a modified Liebig type with rubber bumper caps. All glass parts made of Pyrex glass.

Length, mm.....	300	400	500
Each.....	$1.55	$1.80	$2.00

4942P. OUTER TUBE, ONLY, For Straight-Jacket Condenser, Pyrex. Ends annealed. Free from strain.

Length, mm.....	300	400	500
Each.....	$0.75	$0.90	$1.00

4943P. INNER TUBE, ONLY, For Straight-Jacket Condenser, Pyrex.

For Condenser, Length, mm.....	300	400	500
Each.....	$0.50	$0.60	$0.70

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Editor's Outlook

IT IS hard to keep one's thoughts at home these days. Small wonder, with our aluminum industry going up into thin air—and flying large portions of itself over to Britain, practically on airline schedule; our petroleum industry straining its catalytic innards to produce higher and higher octane aviation gasoline; steel going into tanks and guns; rubber going into protective clothing and army truck tires; every fifth one of our academic chemists going into defense industry or Washington Administration; most of the rest busy on defense research; priorities still keeping the few remaining ones of us from doing a real job of training more chemists to start the list all over again. And in view of all this, incidentally, what's the use arguing whether or not we should get *into* the fight? Much better be thinking what we should do, now we're *here*, wondering when we will get it *over* with—and *then what?*

As teachers, students, chemists—presumably on a moderately high educational stratum of the American Democracy—there are a lot of things we should be thinking about. Probably the world has never been in a situation requiring quite so much, and such concentrated, straight thought. And seldom have the conditions for thinking been so confused. The future course of the world is in the balance. If we don't decide what it shall be someone else will decide it for us—in fact, already *has* decided it, if it can be put over.

"To shoot or not to shoot" is probably the least of our worries. For that, too, may be decided for us. And then some more shooting, until—maybe—we win a war. So what? We won a war before; so what? When you've started the car rolling down hill it is the easiest thing in the world merely to let it roll, until it cracks up at the bottom. But the bottom of the hill probably wasn't where you started out to go, in the first place. And what sort of transportation have you got to the place where you really want to spend the night?

Of course, no one (well, *hardly* anyone—we seem to remember some loud mouthings a while ago) thinks of war as an end in itself. It is a means to an end—of a sort. In the twaddlesome twenties we used to hear it said that "war never accomplishes anything." Bunk! Often, of course, its accomplishment is negative, preventative. But if our wars hadn't been fought the world would undoubtedly be different. It might be *better*—yes—but anyway, different. So if you think *your* war didn't (or doesn't) accomplish anything it is because *you* didn't (or don't) have any clear idea of what you want it to accomplish when you have won it. (Of course, if you haven't *won* it we'll have to start all over!)

And that goes for the future tense, too. *If* we go into this war (let's concede the doubt of it) without a clear idea of what we want it to accomplish we *won't* see that it has accomplished anything, win or lose. And that, we submit, is a more important consideration than our willingness or failure to participate.

We have long been arguing the large part that chemists and chemistry have contributed to the world's welfare. Let us members of this profession—even the young, prospective ones—not shirk our responsibility for the welfare of the world of the future, if it be our privilege to help shape it. At the moment we can only envision what we may want it to be.

Few of us would fight hard to restore the world map of 1935. And to make our efforts worth while we must have something *better* to offer than a consolidated, semi-feudal New Order of Europe with its "burg" in Berlin. But what? We must know what we are after and, if we are sure it is worth the having, be certain we get it.

We don't want a Utopia. Personally, as a matter of fact, we have always thought Utopia a pretty dull-sounding place. But we certainly do want a world in which a fellow can have the reasonable pleasures of life in return for a reasonable contribution from his own resources, mental or physical; in which a fellow can keep his self-respect and the earned respect of his neighbors, regardless of his source or his social or economic standing; in which there will be definite rights of individuals and of groups of individuals; etc. Everyone will have to think what specifications belong in this list. (And by the way, there is one more we would like to be sure to add: no mad dogs, human or canine, will be allowed to run around loose to disturb the peace.)

The last year has seen abundant proof that a war cannot be won by defensive measures alone. There is just as good reason to believe that a satisfactory peace cannot be won that way, either. We must prepare a "peace offensive" before stirring from our homes. It will not be worth while to take what the other fellow gives us. We ought to know, we did it once!

BURKE'S famous speech on conciliation with America contains the equally famous observation that "public calamity is a mighty leveller." The maxim applies to the reaction now in progress in secondary-school science in urban centers.

While the nation rushes to prepare for war under the name of defense, jobs have become plentiful for high-school boys and girls. Some of these jobs are those which would ordinarily be filled by their older brothers, now away at military camp.

(*Continued on page 539.*)

What's Been Going On

We Take 'Em Apart, Then We Put 'Em Together Again

First cotton, to make rayon, and now wool.

WOOL strongly resistant to moths, shrinkage, and alkalies (such as those present in laundry soap), yet retaining the familiar untreated product's softness and warmth, has now been achieved by first learning and then modifying wool's molecular structure. Although fundamental research on the structure of cellulose, the basic constituent of cotton, many years ago resulted in the rayon industry, it has remained for recent work by the research staff of The Textile Foundation to inaugurate such research with wool.

The particular value of wool for clothing, blankets, and carpets, its principal outlets, lies in its unique properties of warmth and its ability to regain its original length or shape after it has been stretched, crumpled, or stepped on. This resilience is really primarily responsible also for its warmth; cotton blankets would be warm as wool if instead of matting together in use they could retain a loose, porous texture, filled with minute insulating air spaces, as do woolens. Wool owes its resilience to a spring-like molecular structure. The molecules of other common fibers resemble a bundle of separate strings, each a long chain of molecules, known as linear superpolymers, consisting, so to speak, of all length and no breadth. In wool, however, these stringy chains are all connected together by short cross chains at frequent intervals, in all three dimensions. Thus, when wool is tugged or pushed, these long molecular chains do not slip against each other into a new equilibrium. Instead, tensions set up by the cross chains restore the wool to its original kinky shape once the external force is removed.

These short cross-chain links, it is now established, are easily destructible. They are wool's Achilles heel, responsible in part for its shrinkage in laundering, edibility by moths, and sensitivity to alkalies. What The Textile Foundation has now done is to take these links apart and react them with chemicals that rejoin the broken links in a form more stable and chemically resistant.

Research on the molecular structure of wool led to the prediction that if wool's weak cross links, chemically known as disulfide or cystine bonds, could be broken down and built up again in chemically stable form, the defects of wool would be eliminated or largely reduced and its desirable properties retained. The work thus far has definitely confirmed this prediction. These disulfide linkages have been broken down in the laboratory with soluble organic sulfur compounds known as mercaptans, of which thioglycollic acid has thus far been found the best. In the same manner, the moth breaks these linkages by its digestive juices and then dissolves the weakened wool by having its digestive tract on the alkaline side. Some wool-rotting microörganisms likewise can accomplish this gastronomic feat, which neither man nor beast can perform. In reconstituting wool, the rupture of the links by thioglycollic acid is followed by treatment with a reagent such as methyl or ethyl dibromide, which reacts with the stumps of the broken cross linkages and rejoins them in a much more stable form. Though any proportion of the links may be reconstituted, alteration of about half of them confers the desired properties.

The final product so obtained is much more resistant to attack by moths, alkalies, enzymes, and bacteria. It retains the original stretch and warmth characteristics, is appreciably more resistant to shrinking after laundering, and has a "feel" very similar to that of untreated wool. Furthermore, it dyes the same as regular wool. Present research activities in this field are being directed to trial of other chemical reagents, speeding up of the reactions, and improvements in the actual processes.

Reconstituted wool will necessarily be more costly than ordinary wool, and hence will initially find application only in special uses where the extra price is warranted. One of the most promising outlets appears to be for felts on paper machines. The chemicals in the water cause gradual deterioration of the felts, and the bacteria and slime hasten spoilage of those in long use. As these felts are large and expensive and shutdowns of the machines are costly, it is hoped that reconstituted wool will not only lengthen their life, but also reduce the number of shutdowns. Subsequently, however, it is anticipated that this new stabilized wool may win a market as well for many types of clothing and household fabrics. Protection against attack by moths and economy of laundering instead of dry cleaning may well tempt many to pay somewhat more for such products.

—From the *Industrial Bulletin* of Arthur D. Little, Inc.

CIVIL SERVICE EXAMINATION FOR SCIENTIFIC AND TECHNICAL AIDS

AN EXAMINATION has just been announced by the Civil Service Commission to recruit technical and scientific aids for various Government agencies. Men and women are needed to do research and testing in metallurgy, fuels, chemistry, physics, explosives, and radio. The positions pay from $1440 to $2000 a year. Persons may qualify who have had *either* appropriate experience or study.

Among the Government agencies that expect to utilize the employment lists set up as a result of this examination are: Bureau of Agricultural Chemistry and Engineering, Department of Agriculture; Bureau of Mines, Department of the Interior; and the Bureau of Standards, Department of Commerce. The War and Navy Departments also have vacancies—the War Department in its Quartermaster Corps; and the Navy in its laboratories.

Applications will be rated as soon as practicable after receipt at the United States Civil Service Commission, Washington, D. C., until June 30, 1942, and certification made as the needs of the service may require. If sufficient eligibles are obtained before the date specified, the receipt of applications may be closed, in which case due notice will be given.

Early Chemistry at Le Jardin du Roi

CLARA DE MILT

H. Sophie Newcomb Memorial College, Tulane University, New Orleans, Louisiana

LE JARDIN du Roi, now called The Museum of Natural History, is a unique institution, for under its superintendence are botanical and zoölogical gardens, several museums, and eighteen professorships in various branches of science. The first two chairs provided for were in botany and chemistry and the lectures and demonstrations in chemistry, almost since their beginning, have had a far-reaching influence on the development of chemistry not only in France but throughout Europe. In the middle of the eighteenth century Rouelle's lectures inspired the young lawyer, Lavoisier, to devote his energies to chemistry; Gay-Lussac and Chevreul held professorships at the Museum and it was in one of these laboratories that Frémy, assisted by the young Moissan, did the fundamental work which led finally to the isolation of fluorine and the invention of the electric furnace.

The first lectures on chemistry given in Paris and open to the public, that is, not a part of the course in medicine at the University of Paris, were the lectures of Jean Beguin in a school of pharmacy established by him with the help of Jean Ribit, first physician to the King, Henry IV, and Turquet de Mayerne. These lectures on pharmaceutical preparations, mainly chemical medicines, accompanied by demonstrations in laboratory technic, probably began in 1604 and continued until the death of Beguin, which occurred about 1620. This practice of public lectures by apothecaries in whose shops laboratory technic was taught to a few students lasted far into the nineteenth century. Among the famous courses offered in chemistry by apothecaries in their own shops may be mentioned those of Nicolas Lemery and Guillaume-François Rouelle, the latter of whom became demonstrator at Le Jardin du Roi in 1742. Following the death of Beguin such a course of lectures in Paris was given by William Davidson, a Scotchman, and when the chair of chemistry was established at Le Jardin du Roi and the laboratories opened in 1640, Davidson became the first demonstrator.

Parallel with this interest in chemical processes as a means of preparing drugs, there developed an interest in the cultivation of medicinal plants, or simples as they were then called from the Latin word *simplicia*, meaning crude drugs or raw materials for their preparation. The very early gardens had been attached to the monasteries but in the sixteenth century private gardens owned or cared for by physicians and/or apothecaries had come into being. Wherever conditions were favorable these private gardens were expanded into public ones and in most instances were connected with a university, the professors of medical subjects using the materials in them for demonstration purposes. Such were the gardens at Basel, Heidelberg, Leyden,

Courtesy of Library of Department of Agriculture
GUY DE LA BROSSE

and Padua, the last mentioned being the oldest of the public gardens, established by the Venetian Republic in the middle of the sixteenth century. Nicolas Houël, having acquired an honorable fortune in his profession of pharmacy, provided for such a garden in Paris in his bequest of 1577. This became the most important of the gardens of the apothecaries of Paris and on the site of it was built later the École de Pharmacie. Henry IV had founded one in 1596 in Montpelier, celebrated at the time for its medical school and its course in pharmacy. In the last quarter of this century, in the private gardens of Jacques Gohory and the elder Guy de la Brosse, are to be found the immediate origins of Le Jardin du Roi. The lectures and laboratories provided for when the garden was opened were the result of the efforts of a group of physicians, for the most part Protestants, who had received their training in medicine not in the University of Paris, but in Montpelier, Basel, and the universities in Germany.

The establishment of the laboratories for experimental work in botany and chemistry and a garden for the growth of medicinal plants may be considered in a sense the outward, material culmination of a movement in France toward empiricism in science, that had its beginnings in the spread of Protestantism and in the

[1] Presented in part before the Division of the History of Chemistry at the 101st meeting of the A. C. S., St. Louis, Missouri, April 9, 1941.

rise of the Protestant academies. The Huguenots, like the Puritans, were methodical, practical, and physically active; they believed that man must use his hands as well as his head. To them contemplation and speculation were associated with idleness; hence the emphasis in their academies was on the utilitarian, rather than on the theoretical aspects of science, and more attention was given to scientific subjects and technology than in the Catholic institutions. It is not surprising, therefore, to find that the first public courses offered in chemistry in Paris were under the direction of Protestants and that their lectures were accompanied by demonstrations.

Le Jardin du Roi, later called Le Jardin des Plantes, since 1792 called Le Musée d'Histoire Naturelle, is situated on the left bank of the Seine not very far from the Sorbonne. Since the early part of the twelfth century this section of the city and the neighboring faubourg St. Victor have been the scene of intellectual activity and scientific experiments. Close by the Museum stands the old abbey of the monks of St. Victor, founded by Louis VI in 1112, whose rich library was a source of inspiration in the thirteenth century and within whose walls the famous Peter Abelard lived. Not far from what was once the good land of the abbey a small river, the Bievre, flowed sluggishly through the marshland to join the Seine toward the north. Up the river on the outskirts of the city Gilles Gobelin established a dye works, about the middle of the fifteenth century, since he had noted that the water of the river possessed properties advantageous to the dyeing art of the time. The enterprising monks of St. Victor a century later turned the small river from its natural course and began to drain the marshland near their domain so that it might be used for cultivation.

In 1572 Jacques Gohory, a member of the legal aristocracy, who had traveled widely in the service of the French ambassadors and who for many years had devoted himself to the study of the natural and occult sciences, especially alchemy, built a laboratory and laid out a garden of simples where the labyrinth of the Museum now is. Gohory was particularly interested in the tobacco plant which had been brought to France from Brazil in 1556. His home was the meeting place of the scientists in Paris and among his friends he numbered Jean Ribit, Joseph Duchesne, and Turquet de Mayerne, physicians, all of whom had studied pharmacy either in Switzerland or Germany and all of whom, including Gohory, were followers of Paracelsus and therefore advocates of the so-called chemical medicines.

It is possible that the idea of a garden in Paris for the growth of medicinal plants, supported by the government, may have originated with Riolan, physician to Marie de Medici, who had seen such gardens in Italy and Germany and who had in 1618 presented a request for one to the University of Paris. But the idea was made a reality by the efforts of three physicians of Louis XIII: Jean Hérouard, Charles Bouvard, and another Guy de la Brosse, grandson of one of the physicians of Henry IV. Of these Guy de la Brosse played the most important part and should be considered as the founder of Le Jardin du Roi. In 1626 he wrote five important letters about its establishment, one of which was addressed to Richelieu. He offered his own estate as part of the grounds, to be added to by the purchase of additional land. To the young King, Louis XIII, to whom Guy de la Brosse had also written, Richelieu proposed this foundation which was authorized by *lettres patentes* in 1626. Edicts of this same year named Hérouard, first physician of Louis XIII, superintendent and Guy de la Brosse intendant. Hérouard died in 1627 and Bouvard took his place. Bouvard was fifty-six at the time and was concerned primarily with his office of first physician and his disputes with the Faculty of Medicine so he turned the entire management of the project over to Guy de la Brosse. The public was apprised of the success of the venture by *La Gazette* of May 2, 1634.

"This past week there was presented to the King by le sieur de la Brosse, one of his physicians, the plan of the garden which His Majesty has had constructed in the faubourg Saint-Victor in Paris for the culture of medicinal plants, the superintendence of which is to be under the jurisdiction of the first physician."[2]

La Gazette was published by Theophraste Renandot, a physician, and M. D. Montpelier, an ardent chemist who sided with the apothecaries in their quarrel with the Faculty of Medicine over the contents, prices, and sale of medical remedies. Incidentally *La Gazette* is said to have been the first newspaper published in France. Richelieu contributed to this weekly largely because of his hatred of the University of Paris. Guy de la Brosse died in 1641 and his body was interred in the chapel which is now a part of the halls of the Museum. He had arranged in 1635 that the son of Bouvard should succeed him. Long after his death, Patin attacked the record of de la Brosse in one of his many letters. Hamy[3] in his study of Guy de la Brosse has concluded that he was a native of Paris and a Protestant. These conclusions have been contested.

The first public lectures on chemistry were sponsored by the physicians and apothecaries in Paris who were followers of Paracelsus and strong advocates of the use of chemical drugs, chiefly compounds of mercury and antimony. It was this group that met at the house and laboratory of Jacques Gohory. The most prominent of them was Jean Ribit or de la Rivière, often called Roch le Baillif, a staunch Calvinist, who, after the accession of Henry IV, had returned to Paris under the protection of le duc de Buillon, ruler of the Sedan, a stronghold of Protestantism. In 1594 he had become the first physician to the King. Ribit believed in the use of preparations of antimony. Joseph Duchesne (Latin, *Quercetanus*) had learned chemistry in Germany and had taken his medical degree at Basel.

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[2] DENISE, "Bibliographie du Jardin des Plantes," Daragon, Paris, 1903, p. 30.

[3] DENISE, *op. cit.*, p. 40.

He had come to Paris in 1593 and his success was immediate. For the Paris of his day Duchesne's knowledge of pharmacy and chemistry was superior and his use of the new preparations netted him a fortune. He favored compounds of mercury, especially mercurous chloride, often referred to in the early seventeenth century as *panchymachogum Quercetani*. Just before 1600 the able Turquet de Mayerne, a native of Switzerland and a Protestant, joined the group. He had studied at Heidelberg and had taken a medical degree at Basel and one also at Montpelier. From Montpelier he had come to Paris to practice, where he soon rose to a position of prominence. Mayerne gave lectures on medicine which were attended mainly by surgeons and apothecaries and in spite of the opposition of the College of Physicians he boldly defended the use of chemical medicines, particularly the use of calomel and a lotion of mercuric salts. In 1603, irritated by an attack against him, he published a pamphlet justifying his remedies with the medical theories and practices of Galen and Hippocrates. But the physicians in Paris unanimously condemned his apology and Mayerne was forced to cease the lectures. He left Paris for England early in 1606 but not before he had, with the help of the popular Ribit, started Jean Beguin off with his public lectures and demonstrations.

An excellent account of Jean Beguin has been written by Professor T. S. Patterson[4] and the information about him and his text given here has been obtained mainly from this article. A native of Lorraine, Jean Beguin was born about the middle of the sixteenth century and received a good classical education. His knowledge of practical chemistry was derived at least in part by observation during his travels through the mining districts of Germany. He took up pharmacy as a profession and came to Paris, possibly from Sedan since he extols the remedies of Nicolas Bonne, the apothecary of le duc de Buillon, friend of Jean Ribit. Beguin established a school of pharmacy and seems to have taught effectively the best processes for preparing drugs, particularly those derived from mineral substances. That his teaching met with opposition is indicated by his remarks in "The Author to the Reader, Salutation" in the 1612 edition of "*Tyrocinium Chymicum*" on "how much odium and envy my friendliness towards, and my ability to promote, the affairs of medicine, have stirred up against me."[5] In 1610 Beguin wrote a little book of seventy pages for the use of his students in order that they might be spared the trouble of copying descriptions. The title reads, "The Chemical Beginner, acquired from the Fount of Nature and Manual of Experience by its Author, who gives and devotes himself and what is his, to God, Thrice best and greatest." The book does not bear the author's name and was printed privately to be distributed by the author himself. A copy, however, found its way to Cologne where it was pirated and reprinted in 1611. Beguin, annoyed by the reprinting of what today would be regarded as a laboratory manual not too carefully written, then corrected, revised, and expanded the book, publishing it in 1612. The first French edition appeared in 1615 and editions continued to be published until 1690. Most of the editions, especially those published outside of France, were in Latin but it was translated into German and English, the London edition appearing in 1669. On account of the large number of editions of the "*Tyrocinium Chymicum*" issued, Beguin's book must have been found to be of great practical value and it seems strange, as Professor Patterson points out, that it has not been singled out for comment and praise by historians of medicine, pharmacy, and chemistry. Hoefer mentions him only as having been protected by Ribit and writes nothing whatever of his book; Kopp does not even mention his name. Beguin's directions are often obscure and his short discussions of processes show the influence of the alchemists of the preceding time, but his alchemy was of a "common sense" type and the man must have been an honest investigator.

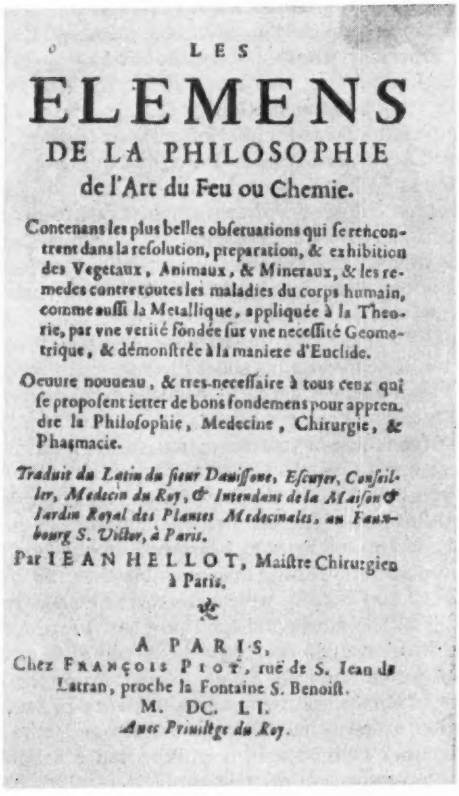
According to Hoefer,[6] William Davidson, a Scotchman, was called to fill the first chair of chemistry at Le Jardin du Roi. The formal opening of the garden and the lecture rooms and laboratories connected with it took place in 1640 but it is possible that lectures on chemistry and botany were held there some years before this. The house and land purchased in the name of the king in 1626 included the estate of Guy de la Brosse, which he must have inherited from the elder Guy de la Brosse, mathematician to Henry IV, who had a garden of rare and delicate simples and who also, like Jacques Gohory, his neighbor, had a laboratory for the investigation of their properties. It is certain that Guy de la Brosse lived in the garden from 1626 on; his nephew, Fagon, who became first physician to Louis XIV about 1680 and by virtue of this office superintendent of the garden and professor of chemistry, was born there in 1638. Hoefer states also that Davidson was lecturing on chemistry during the minority of Louis XIII, which would indicate that he must have begun to lecture in Paris shortly before or after the death of Beguin, about 1620. It seems reasonable to suppose, therefore, that Davidson, a physician interested in pharmacy and the new chemistry of inorganic preparations, had set up a shop in Paris under the protection of the English Protestant group and, following the practice of Mayerne and Beguin, offered lectures with demonstrations to the public. In 1625 Henrietta Maria, sister of Louis XIII, had married Charles I, King of England, the marriage being sanctioned by Richelieu. Davidson, practicing among the prosperous English and Scotch aristocracy living in Paris, with a reputation established by his lectures, may have purchased his post at the garden and also his office as one of the king's physicians. Such transactions were not uncommon in France at this period

[4] PATTERSON, "Jean Beguin and his '*Tyrocinium Chymicum*,'" *Ann. Sci.*, **2**, 243–98 (July, 1937).

[5] PATTERSON, *op. cit.*, p. 253.

[6] HOEFER, "Histoire de la chimie," Didot Frères, Paris, 1869, Vol. 2, p. 234.

and later. Davidson, appointed during the administration of Guy de la Brosse, must have been acceptable to Vautier, a strong advocate of chemical medicines.



LES

ELEMENS

DE LA PHILOSOPHIE

de l'Art du Feu ou Chemie.

Contenans les plus belles obſeruations qui ſe rencontrent dans la reſolution, preparation, & exhibition des Vegetaux, Animaux, & Mineraux, & les remedes contre toutes les maladies du corps humain, comme auſſi la Metallique, appliquée à la Theorie, par vne verité fondée ſur vne neceſſité Geometrique, & démonſtrée à la maniere d'Euclide.

Oeuure nouueau, & tres-neceſſaire à tous ceux qui ſe propoſent ietter de bons fondemens pour apprendre la Philoſophie, Medecine, Chirurgie, & Phaſmacie.

Traduit du Latin du ſieur Daniſſone, Eſcuyer, Conſeiller, Medecin du Roy, & Intendant de la Maiſon & Jardin Royal des Plantes Medecinales, au Fauxbourg S. Victor, à Paris.

Par IEAN HELLOT, Maiſtre Chirurgien à Paris.

A PARIS,

Chez FRANÇOIS PIOT, rue de S. Iean de Latran, proche la Fontaine S. Benoiſt.

M. DC. L I.

Auec Priuilege du Roy.

Courtesy of the Harvard Library

TITLE PAGE OF THE 1651 FRENCH EDITION OF DAVIDSON'S TREATISE

Vautier, after the death of Richelieu in 1642, had become first physician to the young king, Louis XIV, then five years old. At the time he became the first physician and therefore administrator of the garden, Bouvard de Fourqueux, son of the older Bouvard, was the superintendent. Bouvard, who refused to resign his post despite the decrees of the Parlement of Paris passed in 1647, remained as actual administrator until the time of Vallot. All that remained of power to Vautier was the appointment of the demonstrators.

If one can believe some of the reports of the garden at this time it appears to have been neglected during the administration of Vautier, which covers most of the period of Davidson's lectures. But the neglect could not have been serious by the year 1644 if the account of John Evelyn is accepted.

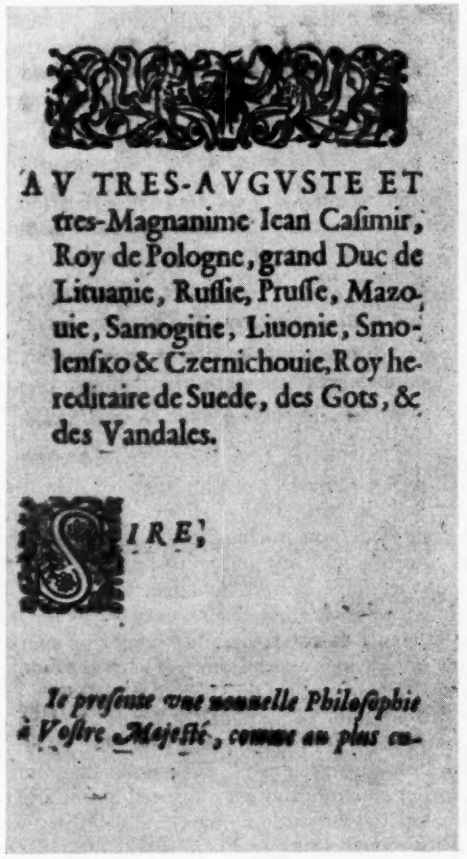
"I took coach and went to see the famous Jardine Royale, which is an enclosure walled in, consisting of all varieties of ground for planting and culture of medicinal simples. It is well chosen, having in it hills, meadows, wood and upland, natural and artificial and is richly stored with exotic plants. In the middle of the *parterre* is a fountain. There is a very fine house, chapel, laboratory, orangery and other accommodations for the President, who is always one of the king's chief physicians."[7]

Vautier, however, was much more interested in the lectures than in the plants for it was he who substituted a course in anatomy for one given on the interior of plants. This is the period of the quarrel between the medical faculty of the University of Paris, led by the able and vitriolic Guy Patin, and the physicians and apothecaries not connected with the University. When Vautier died in 1652 Patin pronounced him a victim of his own antimonial prescriptions.

Davidson remained at Le Jardin du Roi during part of the administration of Vallot, Vautier's successor. His lectures attracted large audiences. On September 21, 1649, John Evelyn again visited the garden, "went to hear Dr. D'Avinson's lecture in the physical garden and see his laboratory, he being the Prefect of that excellent garden and Professor Botanicus."[8]

[7] "Diary of John Evelyn," Henry Bohn, London, 1859, Vol. 1, p. 53.

[8] "Diary of John Evelyn," *op. cit.*, p. 263.



AV TRES-AVGVSTE ET tres-Magnanime Iean Caſimir, Roy de Pologne, grand Duc de Lituanie, Ruſſie, Pruſſe, Mazouie, Samogitie, Liuonie, Smolenſko & Czernichouie, Roy hereditaire de Suede, des Gots, & des Vandales.

SIRE,

Ie preſente vne nouuelle Philoſophie à Voſtre Majeſté, comme au plus cu-

Courtesy of the Harvard Library

DEDICATION OF THE 1651 FRENCH EDITION OF DAVIDSON'S TREATISE

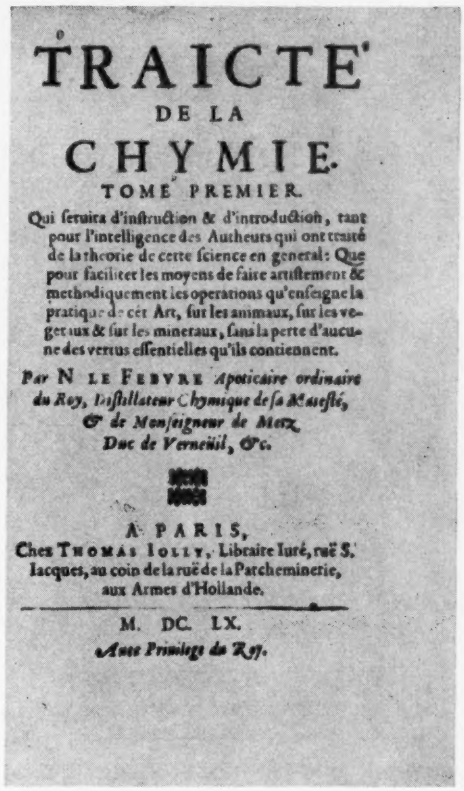
Among those impressed by the learning and ability of Davidson was John Casimir who became King of Poland in 1648. Sometime in 1650 Davidson resigned his post to become physician and investigator of the mysteries of the art of fire to this John Casimir, as is shown by the dedication of the first French translation of Davidson's book, published in 1651. Davidson's last book was published in Holland in 1660. There is said to be a portrait of him at the age of sixty-nine in the British Museum copy of the complete 1640 edition of his "*Philosophia pyrotechnia.*"

Davidson in 1635 published in Latin a work entitled, "*Philosophia pyrotechnia, seu Cursus chymiatricus.*" It is divided into four parts. Parts Three and Four seem to have appeared first. Part Three is devoted to speculative theories and shows his knowledge of the ancient philosophers; Part Four treats of chemical operations. Parts One and Two are dedicated to James and George Stuart. In 1640 a second edition was published and editions appeared in 1642, 1644, and 1657. It was translated into French in 1651 by Jean Hellot, a master surgeon of Paris, a second edition of this French edition appearing in 1657. In 1675 another French edition appeared, translated from the Latin by the author himself. A glance at the title page of the 1651 French edition will give the reader some idea of the book.

Title: "The Elements of the Philosophy of the Art of Fire or Chemistry. Containing the most wonderful observations which are found in the resolution, preparation and exhibitions of Vegetables, Animals, and Minerals, and the remedies against all the maladies of the human body, as also the Metallic, applied to the Theory, truly founded on a necessary Geometry and demonstrated in the manner of Euclid. A new work, and very necessary to all those who propose to master the foundations in order to learn Philosophy, Medicine, Surgery, and Pharmacy."

Most of the book is taken up with theory rather than with chemical processes and the directions for the preparations are often confused. Mineral, vegetable, and animal substances are discussed but not in any logical order. For example, Chapter XXIX treats of flowers of antimony and is followed by Chapter XXX on flowers of benzoin—storax from the trees of India, which he says flourish well in the Royal Garden of Plants. Chapter XXXI deals with corrosive sublimate and is followed shortly by Chapter XXXIII on the spirit and oil of honey. Chapter XL is concerned with the calcination of metals. As the example of calcination, the author selects that of lead and describes the process, indicating that the procedure is based on a pound of lead. But no weight of the product formed is given.

Shortly after the departure of Davidson, Vallot appointed Nicolas Le Fevre, also a Protestant, as demonstrator in chemistry. Antoine Vallot had not taken his degree at the University of Paris but had established himself in Paris as first physician to the queen regent, Anne of Austria, and as a friend of Nicolas Fouquet who had risen to power in 1650. According to the not too reliable Patin, Vallot purchased his office as first physician to the king and administrator of the garden from Mazarin for 30,000 francs. Like Vautier, Vallot adopted the use of the new remedies, namely, preparations of antimony, particularly antimonial wine, cinchona, and laudanum, which brought upon him the maledictions of the Faculty of Medicine. Their accusations toned down for a short period after 1658 when Louis XIV, then twenty years old, recovered



TRAICTE'
DE LA
CHYMIE.
TOME PREMIER.

Qui ſeruira d'inſtruction & d'introduction, tant pour l'intelligence des Autheurs qui ont traité de la theorie de cette ſcience en general: Que pour faciliter les moyens de faire auſſi ſement & methodiquement les operations qu'enſeigne la pratique de cét Art, ſur les animaux, ſur les vegetaux & ſur les mineraux, ſans la perte d'aucune des vertus eſſentielles qu'ils contiennent.

Par N LE FEBVRE *Apoticaire ordinaire du Roy, Diſtillateur Chymique de ſa Maieſté, & de Monſeigneur de Metz, Duc de Verneüil, &c.*

A PARIS,
Chez THOMAS IOLLY, Libraire Iuré, ruë S. Iacques, au coin de la ruë de la Patcheminerie, aux Armes d'Hollande.

M. DC. LX.
Auec Priuilege du Roy.

Courtesy of the Harvard Library

TITLE PAGE OF THE 1660 FRENCH EDITION OF LE FEVRE'S TREATISE

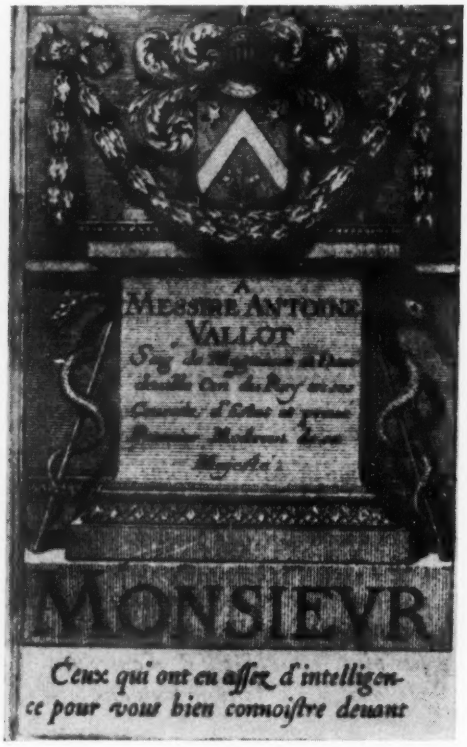
from a serious illness at Calais after the administration of antimonial wine by Vallot. But many charges continued to be brought against him and his unpopularity with the conservative medical practitioners lasted until his death. Madame de Sévigné, writing to her daughter in February, 1671, indicates the feeling against Vallot at the time:

"This year nothing comes to Perfection not even Monsieur Vallot's Indisposition. He is much mended; and instead of tipping off, as I was assured he would, he has taken a certain Pill which has brought him to Life again."[9]

Vallot died at the garden August 9, 1671, at the age of seventy-seven. During the first years of his administration he neglected the plants so that some of the rare simples died, but in 1658 his interest was aroused and

[9] CURLL, "Court secrets," London, **1727**, p. 3.

he sent Fagon, nephew of Guy de la Brosse, in search of plants to replace them. For the remainder of his administration he devoted much of his energy to the upkeep of Le Jardin du Roi even though certain of his acts merit censure: Colbert noted on a visit after Vallot's death that ground intended for rare plants had on it vines for the use of the administrators.



Courtesy of the Harvard Library

DEDICATION OF THE 1660 FRENCH EDITION OF LE FEVRE'S TREATISE

Many years before his appointment to the chair of chemistry at the garden in 1652, Nicolas Le Fevre must have settled in Paris where he operated an establishment of his own in which he prepared medicines and gave lectures. John Evelyn records on January 18, 1647:

"The 18th. I frequented a course of Chemistry, the famous Monsieur Le Febure operating upon most of the nobler processes."[10]

In the letter to the apothecaries of France in his book published in Paris in 1660 and in a similar letter addressed to the apothecaries of England in the English translation of 1664, Le Fevre speaks of his training and of his devotion to the art of pharmacy. He was instructed by his father, an apothecary, "most exact, who employed himself particularly in the curious searches into things necessary for the Election, Preparation, and Composition of Medicines, which he kept in his Shop. . . ."[11] Le Fevre tells us also that he had been working in pharmacy for thirty-five years which makes him a man of over forty when he became demonstrator. After the death of his father he lived in Sedan where he was instructed by "one Dr. Duhan, deceased, Dr. of Physick, and Professor of Philosophy." From here he went to Paris where he

"had the happinesse of Liberty to converse with M. du Clos[12] Dr. of Physick, who did me the favour to correct my defaults . . . . I was called some years since by the favour of Mons. Vallot . . . as Apothecary and Distiller in ordinary to the King, to perform by his precepts and order lessons and operations in a course of the true Pharmacy, which is Chymistry, and that in the Garden which his Majesty prepared in the suburbs of St. Victor. 'Twas there truly that I found wherewithall to satisfie the appetite of my curiosity, not only by the profuse expence with which this True Father and Restorer of Medicine and Chymistry furnisht us vessels and materials withal, for the demonstration of those operations which I was commanded to make yearly, as well after the Ancient as new wayes."

Invited by Charles II to England to become professor of chemistry to the King, Le Fevre left France in 1660. Barriers directed against Protestants in the professions and in business had begun to be raised in Paris and in the provinces and Le Fevre chose to accept a smaller post in a foreign country because it offered him and his family freedom in the exercise of their religion and security in his profession. He became apothecary in ordinary to the royal household December 31, 1663. From 1664 to 1666 he was entrusted with the laboratory at St. James's Palace. On May 20, 1663, Le Fevre had been elected a fellow of the Royal Society. He died in the parish of St. Martin-in-the Fields, London, in the spring of 1669.

Le Fevre's "Traicté de la Chymie" in two volumes was published in Paris in 1660 after his departure for England and is dedicated to Monsieur Vallot. A second French edition appeared in 1669, followed by other editions, the fifth being printed in 1751 in five volumes. An English translation made by "P. D. C. Esq. one of the Gentlemen of his Majesties Privy Chamber" was published in London in 1664, to be followed by another edition in 1670 also printed in London. It was translated into German, being published at Nürnberg in 1676, and a French edition was printed at Leyden in 1669. Le Fevre also published in London in 1665 "Discours sur le grand cordial de S[r] Walter Rawleigh," the English version of which had appeared the year before, and translated into French Sir Thomas Browne's "*Religio Medici*" published at The Hague in 1688. Le Fevre published his treatise in French

"because I would imitate the most eminent Authors of Germany, who thought themselves obliged to write of Chymical Pharmacy in the vulgar Tongue, that it might likewise be useful

[10] "Diary of John Evelyn," *op. cit.*, p. 252.

[11] LE FEBURE, "A compleat body of chymistry," Thomas Ratcliffe, London, **1664**.

[12] Probably Samuel Cottereau Duclos, ordinary physician to Louis XIV, who was appointed to the Academy of Sciences at Paris in 1666 as chemist. The French Academy published several of his papers on the contents of mineral waters.

not only to the Apothecaries, but, that it might likewise be serviceable to men of other professions."

Hoefer gives an excellent summary of Le Fevre's work[13]; he recognizes Le Fevre as an able and experienced apothecary and speaks of him as the model of the chemists of the second half of the seventeenth century. In the letter to the apothecaries, Le Fevre points out the value of observation and experiments but his book proves that for the most part he was a speculative chemist. This is well illustrated in the preliminary discourse of the first book of his treatise where he writes in answer to the query should chemistry be called an art or a science:

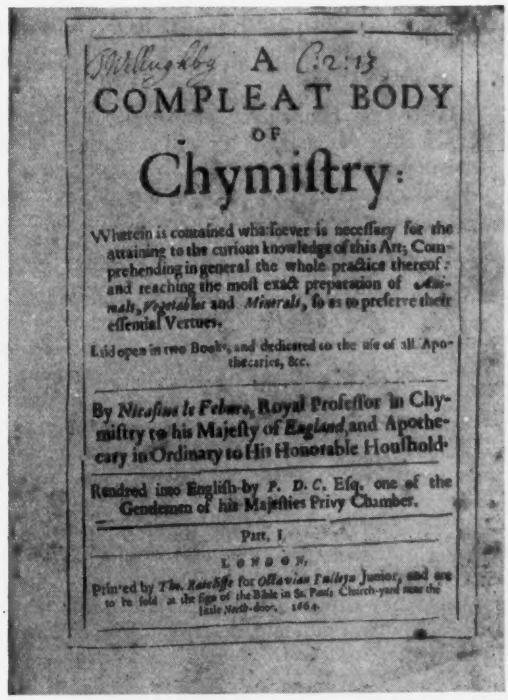
There are "three species of Chymistry; the one wholly Scientifical and given to Contemplation and may well be tearmed Philosophical . . . . The second species of Chymistry may be called Iatrochymistry or Medicinal Chymistry, whose only end is operation . . . . The third species is Pharmaceutical Chymistry, which hath its end only in operation."

Later on he says that,

"Operation is truely the general end of Chymistry . . . . For it is not a Gown or degrees taken in Universities, which constitute the Physician but a solid knowledge of Nature grounded upon Sound Reason and mature judgement improved by practice and experience."[14]

One can agree with Dumas[15] that the treatise is carefully written and that the author has followed a definite order but a study of the table of contents will indicate that the order is not one that reflects clear thinking and originality on the part of Le Fevre who, like Davidson, places the emphasis on the physical state of the substance rather than on the relationships of like substances. A large proportion of the book is devoted to theory, seventy-one pages of Part I of the first English edition being given over entirely to speculation, to say nothing of the theoretical introduction to each division of each chapter. Chapter V of the second book of Part II, "Of Dew and Rain," is characteristic:

"It will suffice to say, that Rain-water must be gathered from the beginning to the twentieth of March (or eight dayes before the Equinoxe, and eight dayes after) because then the Air is all filled and impregnated with those true heavenly seeds that are destined to the renewing of all natural productions."[16]



A
COMPLEAT BODY
OF
Chymistry:

Wherein is contained whatsoever is necessary for the attaining to the curious knowledge of this Art; Comprehending in general the whole practice thereof: and reaching the most exact preparation of *Animals, Vegetables* and *Minerals*, so as to preserve their essential Vertues.

Laid open in two Books, and dedicated to the use of all Apothecaries, &c.

By *Nicasius le Febure*, Royal Professor in Chymistry to his Majesty of *England* and Apothecary in Ordinary to His Honorable Houshold.

Rendred into English by *P. D. C.* Esq. one of the Gendemen of his Majesties Privy Chamber.

Part. I.

LONDON,

Printed by *Tho. Newcomb* for *Octavian Pulleyn* Junior, and are to be sold at the Sign of the Bible in St. Pauls Church-yard near the little North-door. 1664.

Courtesy of the Harvard Library

TITLE PAGE OF THE FIRST ENGLISH EDITION OF LE FEVRE'S TREATISE

A short time after Le Fevre resigned his position at Le Jardin du Roi, Vallot chose as his successor an able, experienced physician and apothecary, Christopher Glaser, a native of Basel, whose excellent short treatise of laboratory preparations first published in 1663 ranks with the best of the few practical books on chemistry of the seventeenth century. A comparison of any of the editions of Glaser's treatise with one of the early editions of Lemery's treatise will show that Lemery's model was Glaser's book.

[13] HOEFER, *op. cit.*, **1869**, Vol. 2, pp. 278–81.
[14] LE FEBURE, *op. cit.*, p. 7.
[15] DUMAS, "Leçons sur la philosophie chimique," Gauthier-Villars, Paris, **1878**, p. 58.
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An Experiment in Electrical Calorimetry

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WHILE thermochemistry as a branch of physical chemistry can hardly be said to have declined in importance, most of the laboratory manuals of physical chemistry published in recent years have devoted a steadily diminishing amount of space to thermochemical measurements. Perhaps this is because some of the experiments formerly in vogue were so simplified, contained so many approximations, and ignored so many corrections that they provided little or no training in manipulation and could not command the respect of the student. At the other extreme there were experiments, calling for all the necessary corrections, which were so complex and time-consuming that few students, however conscientious, could obtain reasonably good results without devoting an altogether excessive amount of time to the work.

Modern developments in electrical calorimetry enable most of the bothersome corrections inseparable from the older methods to be eliminated, and at the same time they utilize a principle of the utmost simplicity.[2] The work herein described was undertaken with the object of working out a procedure based on up-to-date methods which would be capable of giving reasonably good results in a reasonable time, and yet simple enough for the object of the experiment and the principle of the method to be left clearly in the mind of the student.

PRINCIPLE OF THE METHOD

The reaction to be studied is carried out in a Dewar flask and the accompanying temperature change is noted. If the reaction is endothermic the temperature falls. When the reaction is complete, the contents of the calorimeter are brought back to the initial temperature by the passage of a measured amount of electrical energy through a heating element mounted in the calorimeter. This quantity of energy is, to a close approximation, equivalent to the heat absorbed during the reaction. If the reaction is exothermic, the temperature increases. In this case, when the reaction is over the calorimeter is cooled and then reheated through the same interval of temperature by a measured amount of electrical energy.

Thus, in either case, the heat of reaction is compared directly with a known amount of electrical energy. The water equivalent of the calorimeter vessel and fittings nowhere appears in the procedure so that a most troublesome quantity is completely eliminated. Furthermore, if the reaction is exothermic and if the rate at which the electrical energy is supplied is made such that the electrical heating takes the same length of time as did the chemical heating, then the radiation and stirring corrections also disappear. With an endothermic reaction, the heat of stirring opposes the chemical cooling and assists the electrical heating so that it does not cancel, and the same is true of the effect of radiation. However, these corrections can generally be neglected if the vacuum flask is a good one and the stirring not too violent; or else they can be determined and allowed for. Finally, it will be noted that the thermometer is used primarily for reproducing a temperature interval rather than for measuring it, and errors in the calibration of the thermometer do not affect the result.

DESCRIPTION OF THE APPARATUS

The calorimeter vessel is a straight-sided Dewar flask of about 5-cm. inside diameter. Supported within it are the following pieces of equipment.

1. A Stirrer.—This consists of a two-bladed glass propeller of about 15-mm. diameter, made by sealing a short length of glass rod across the end of a longer rod and flattening the ends of the crosspiece to make the blades. It is driven by a small electric motor.[3]

2. An Electric Heater.—This is of the type suggested by Bury and Davies.[4] It consists of a U-shaped, thin-walled glass capillary tube filled with mercury. (See Figure 1 (*A*).) The mercury must be dry—in order to prevent bubbles of vapor breaking the mercury thread when the current passes. This type of heater has the advantage of being easily made, corrosion-proof, and compact, but it is rather fragile. The constricted part must, of course, be completely immersed in the calorimeter liquid.

3. A Reagent Container.—This consists simply of a glass tube of about 20-mm. diameter, flared at the top and closed at the bottom by a cork or rubber stopper. The stopper is bored part way through to hold a glass rod. (See Figure 1 (*B*).) The reagent of smaller volume is placed in this tube with the other solution outside. When it is desired to start the reaction, the stopper is held against the bottom of the calorimeter with the glass rod and the tube drawn away from it slightly so that the contents of the tube can mix with the liquid outside. If the stopper is not attached to the glass rod it may become entangled with the stirrer and break the heating element.

4. A Cooling Device.—This is not ordinarily necessary with endothermic reactions, but is used with exo-

[1] Present address: School of Graduate Studies, University of Toronto, Toronto, Ontario, Canada.

[2] See ROSSINI, "Modern thermochemistry," *Chem. Rev.*, **18**, 233 (1936).

[3] The Model 1, Variable Speed Stirrer, made by the Eastern Engineering Company of New Haven, Connecticut, is especially suitable.

[4] BURY AND DAVIES, *J. Chem. Soc.* (London), 2413 (**1932**).

thermic reactions for cooling the contents of the calorimeter after the reaction is over. Its construction is shown in Figure 1 (*C*). In use, a little ether is pipetted into it and a current of air is drawn through

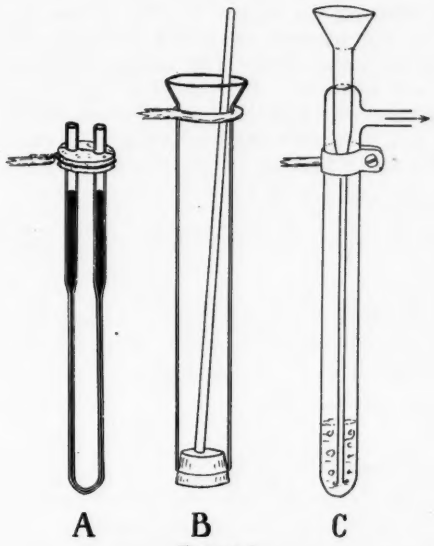

FIGURE 1

The holder for the heating element (*A*) is made from a disc of cork, perforated with two holes and cut into two semicircles. The two halves are bound round the heater with a wire whose ends are twisted together and soldered to a piece of stiff wire. The reagent tube (*B*) is supported in a simple loop of stiff wire. The cooling tube (*C*) is held by a set-screw in a metal collar soldered to a length of wire

with a filter pump to evaporate the ether and cool the calorimeter. All the ether must, of course, be evaporated as otherwise some of the electrical energy will be used in volatilizing the residue. About 5 ml. of ether will cool the calorimeter and 250 ml. of solution 1°C.

5. *A Thermometer.*—A Beckmann thermometer may be used, but results nearly as good can be obtained using a thermometer graduated in tenths of a degree.

Since all these fittings must be packed into the small space provided by the Dewar flask, it is advisable to make special holders for them such as those suggested in Figure 1. If they are attached by clamp holders to a ring stand whose rod will unscrew, then the flask can be removed, without disturbing the fittings, by giving the rod a quarter turn. (See Figure 2.)

The current used for heating is best taken from a storage battery. Since the heating elements generally have a resistance of 5 to 15 ohms, a potential of one to two volts is sufficient to heat the calorimeter at a rate of 0.05° to 0.1° per minute. The current supplied will be more nearly constant if three cells of a lead storage battery are connected in parallel. When current is first drawn from a storage battery, there is a fairly rapid initial fall in potential after which the potential remains very nearly constant for a considerable time. It is therefore advantageous to connect the battery to a double-pole, double-throw switch so that the battery can be drained through a resistance equal to that of the calorimeter circuit for at least 15 minutes before commencing the electrical heating. (See Figure 3.) If this is done, then when the switch is quickly thrown to the calorimeter circuit, the battery is already in a steady state and heat is supplied to the calorimeter at a practically constant rate.

The input of electrical energy into the calorimeter is determined by measuring the current through the heater and the potential across it. This can be done with a voltmeter and ammeter connected as shown in Figure 3 (*A*). If more exact results are desired, a potentiometer can be used as shown in Figure 3 (*B*). The potentiometer is used to measure, first, the potential across the heating element and then the potential drop in a known resistance placed in series with the heater. From this second measurement the current is calculated using Ohm's law.

PROCEDURE

The following is an outline of the procedure followed in studying an exothermic reaction. The modifications necessary when the reaction is endothermic scarcely need to be described in detail.

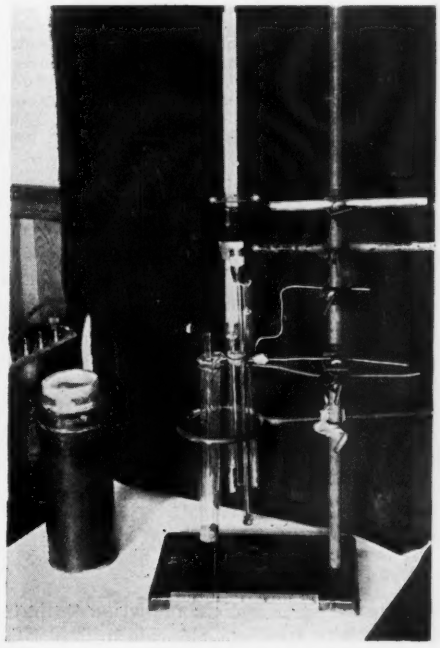

FIGURE 2

The necessary solutions having been prepared and measured out into the calorimeter vessel and reagent container, the stirrer is started, and the apparatus allowed to come to a uniform temperature. A series of temperature and time readings are then taken for

about 10 minutes, after which the reaction is started in the way already described. Observations of temperature and time are continued while the reaction is proceeding and for ten minutes or more after it is over.

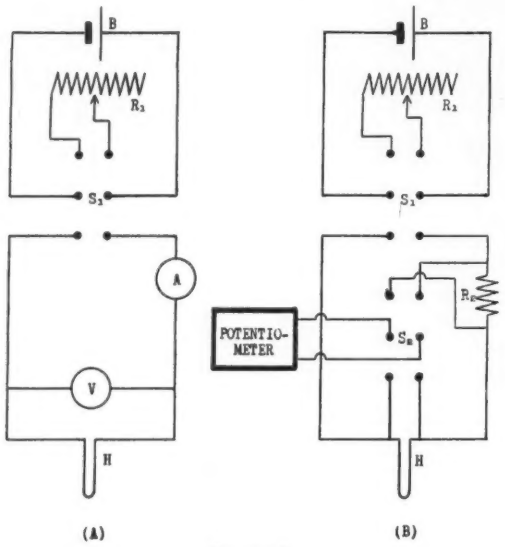

FIGURE 3

By means of the double-pole, double-throw switch S_1, the battery B may be connected either to the draining resistance R_1 or to the heating element H. In circuit (A) the energy dissipated in the heating element is measured with the ammeter A and the voltmeter V. In circuit (B) the energy is measured by connecting the potentiometer through the double-pole, double-throw switch S_2 alternately to the standard resistance R_2 and the heating element H

These readings are plotted as shown in Figure 4. Ether is then introduced into the cooling device and the calorimeter is cooled to a point somewhat below the initial temperature. The battery, which has meanwhile been draining through the resistance, is now connected to the heating element and a new series of temperature and time readings is taken, together with the necessary measurements of current and voltage. This heating curve is plotted on the same sheet as the one previously obtained, and the time required for the electrical heating to duplicate the chemical heating is picked off as shown in Figure 4.

The method of calculating the results will be clear from the example given in the next section.

RESULTS

The reaction studied was the reduction of dilute ferric chloride by dilute stannous chloride in 2 N HCl solution.

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

In the reagent tube were placed 30 ml. of an approximately 0.3 M solution of stannous chloride which was 2 N with respect to hydrochloric acid. The outer vessel contained 200 ml. of 2 N hydrochloric acid and 20 ml. of approximately 0.5 M ferric chloride solution also 2 N in HCl. These amounts provide for an excess of stannous chloride and at these concentrations the heat of dilution of the stannous chloride was found to be negligible. If necessary it could have been measured and allowed for.

The following are typical results of two runs. In Run A a thermometer graduated to 0.1°C. was used and the electrical energy was measured with a voltmeter and ammeter. In Run B, a Beckmann thermometer was used and the energy was measured with a Leeds and Northrup Student's Potentiometer. The results of Run B were used in plotting Figure 4.

Reagents	*Run A*	*Run B*
$SnCl_2$, 30.0 ml.	0.3000 M	0.3000 M
$FeCl_3$, 20.0 ml.	0.4713 M	0.4909 M
HCl, 200 ml.	2.0 N	2.0 N
Readings		
Initial temperature	21.20°C.	21.630°C.
Final temperature	21.65°C.	22.050°C.
Time of electrical heating	660 sec.	920 sec.
Heater voltage	2.05 volt	1.818 volt
Heater current	0.31 amp.	0.2629 amp.
Cal. per 20 ml. $FeCl_3$ soln.	$\frac{2.05 \times 0.31 \times 660}{4.185}$	$\frac{1.818 \times 0.2629 \times 920}{4.185}$
	= 100.2 cal.	= 105.1 cal.
ΔH per mol of $FeCl_3$	$\frac{-100.2 \times 1000}{20 \times 0.4713}$	$\frac{-105.1 \times 1000}{20 \times 0.4909}$
	$= -1.06 \times 10^4$ cal.	$= -1.070 \times 10^4$ cal.

A duplicate of Run B gave 1.064×10^4 cal.

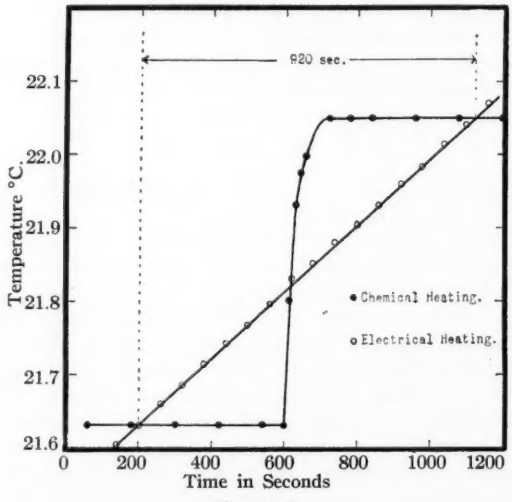

FIGURE 4

Using data for the heats of formation and solution given in the literature[5] the heat of this reaction per mol of ferric chloride at high dilution in water is calculated to be

$$\Delta H = -1.062 \times 10^4 \text{ cal.}$$

in good agreement with the values found above.

[5] HODGMAN AND HOLMES, Editors, "Handbook of chemistry and physics," 24th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, **1940**.

SUMMARY

A technic is described whereby thermochemical measurements can be made with a precision of one per cent or better. The procedure is based on modern electrical methods of calorimetry and is simple enough to be fully understood by undergraduates and should have considerable instructional value. Results are quickly obtained and the cost of the apparatus is moderate.

A CONVENIENT EXTRACTOR FOR USE WITH LARGER QUANTITIES OF PLANT MATERIAL

R. C. BURRELL and ALVIN C. WOLFE *The Ohio State University, Columbus, Ohio*

IN CONNECTION with a study which demanded a rather comprehensive analysis of green soybeans, it became necessary to devise an inexpensive apparatus which would serve for the quantitative extraction of the bean samples with alcohol.

The bottom of a two-quart metal can was pierced with $^1/_8$" holes and covered with filter paper. The macerated beans were placed in the can, which was then supported with inverted porcelain crucibles, about one inch above the bottom of a $6^3/_8$" × $8^1/_2$" glass battery jar. A cylindrical rubber gasket, cut from an inner tube, was stretched around the rim of the jar and a metal lid $6^1/_2$" in diameter with a $^1/_2$" flange was pushed down over this so as to form a leak-proof joint. Soldered around a hole cut in the middle of the lid was a short length of a metal cylinder $1^1/_4$" in diameter into which was fitted a foil-covered cork carrying a glass adapter, the top of which was connected to an ordinary condenser. A second small, metal-jacketed condenser may be used to advantage around the base of the adapter. By means of a glass tube, the side arm of the adapter was connected to a six-liter flask which was placed in a steam bath. The top of the neck of this flask was about level with the bottom of the battery jar, the latter being set on a support attached to a heavy ring stand. On the side of the battery jar near the bottom, a $^3/_8$" hole had been bored through which a siphon of small bore tubing was connected with the six-liter flask. The top of the siphon was level with the maximum height of the sample in the inner container.

As the alcohol was slowly distilled, it condensed and dripped on the macerated beans, gradually seeping through them and through the filter paper and filling the jar to the level of the top of the sample before it siphoned back. Approximately five liters of alcohol were used in operating this extractor. With but little attention the alcohol siphoned back about six times in eight hours. When heating was stopped before extraction was complete, care was taken to have the beans almost covered with alcohol, *i. e.*, the alcohol level not quite up to the top of the siphon. At the end of four days, during which the apparatus was in actual operation for thirty-two hours, tests showed no further extraction of solutes from the beans. The residue was then removed, dried, and weighed; and the residue and extract were separately analyzed.

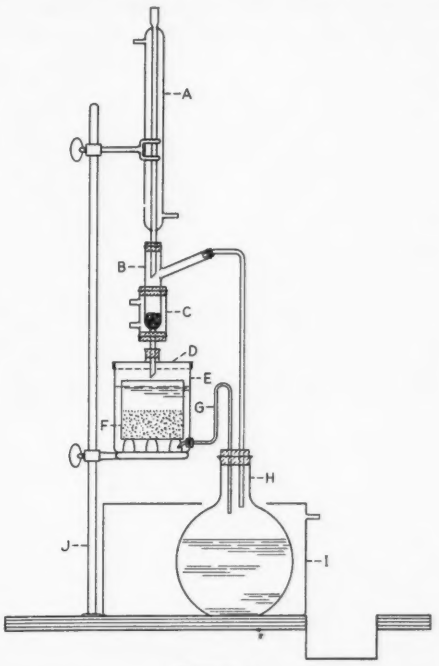

FIGURE 1

A—Condenser. *B*—Adapter with glass wool filter. *C*—Small condenser. *D*—Metal lid with rubber gasket. *E*—Battery jar with $^3/_8$" hole near bottom. *F*—Metal can, bottom pierced with $^1/_8$" holes. *G*—Siphon of small bore or capillary glass tubing. *H*—Six-liter flask. *I*—Steam bath. *J*—Heavy ring stand

An advantage of this extractor over many of the others that have been suggested is that it is very easy to remove the extracted residue quantitatively. In analysis and in the isolation of various plant components, this apparatus has proved suitable for the extraction of a wide variety of plant materials. Furthermore, it has the added advantage of being quite inexpensive.

Relationships between Standard Electrode Potentials of the Elements and Their Positions in the Periodic Table

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PALMAER[1] has shown that a periodicity is exhibited by the curves obtained when standard electrode potentials of the elements are plotted against their atomic weights. Thomlinson[2] has also noted the periodicity of this property. Further relationships existing between the standard electrode potentials of the elements and their positions in the periodic table will be developed here.

The values for E^0, the standard electrode potential, used in this paper (Table 1) are taken from Latimer.[3] The value for the hydrogen electrode is chosen as zero; a positive value of E^0 indicates that the reduced form of the couple is a better reducing agent than hydrogen. All dissolved substances are at an activity of one molal; all gases are at a fugacity of one atmosphere. Potentials are given for a temperature of 25°C. The particular change of valence involved in the electrode reaction is indicated in the table.

TABLE 1

Element	E^0	*Valence Change*	*Group in Periodic Table*
H	0.0000	1	x
Li	3.02	1	IA
Na	2.712	1	IA
K	2.922	1	IA
Rb	2.99	1	IA
Cs	3.02	1	IA
Cu	−0.522	1	IB
Ag	−0.7995	1	IB
Au	−1.68	1	IB
Be	1.70	2	IIA
Mg	2.34	2	IIA
Ca	2.87	2	IIA
Sr	2.89	2	IIA
Ba	2.90	2	IIA
Zn	0.7620	2	IIB
Cd	0.4020	2	IIB
Hg	−0.854	2	IIB
Al	1.67	3	IIIA
Sc	*c.* 2.0	3	IIIA
Y	*c.* 2.1	3	IIIA
La	2.37	3	IIIA
Ga	0.52	3	IIIB
In	0.340	3	IIIB
Tl	0.3363	1	IIIB
Ti	1.75	2	IVA
Th	*c.* 2.06	4	IVA
Sn	0.136	2	IVB
Pb	0.126	2	IVB
V	1.5 ± 0.3	2	VA
Cb	*c.* 1.1	3	VA
Cr	0.71	3	VIA
Mo	*c.* 0.2	3	VIA
W	<0.05	3	VIA
U	*c.* 1.7	3	VIA
S	0.508	−2	VIB
Se	0.78	−2	VIB
Te	0.92	−2	VIB
Mn	1.05	2	VIIA
F	−2.85	−1	VIIB
Cl	−1.3583	−1	VIIB
Br	−1.087	−1	VIIB
I	−0.5345	−1	VIIB
Fe	0.440	2	VIII
Co	0.277	2	VIII
Ni	0.250	2	VIII
Ru	*c.* −0.45	2	VIII
Rh	*c.* −0.6	2	VIII
Pd	−0.83	2	VIII
Os	*c.* −0.7	2	VIII
Ir	<−1.0	2	VIII
Pt	*c.* −1.2	2	VIII

From the values of E^0 in Table 1, the following rules can be derived:

1. Any member of an A family has a greater algebraic value of E^0 than has any member of a B family. Exceptions are chromium, molybdenum, and tungsten.
2. Any member of an A family has a greater algebraic value of E^0 than has any member of Group VIII. Exceptions are molybdenum and tungsten.
3. In the A family of each of the first three groups, E^0 increases in algebraic value with an increase in atomic number. Lithium is an exception.
4. In the B family of each of the first three groups, E^0 decreases in algebraic value with an increase in atomic number.
5. In the A families of each of the first two groups, an element has a greater algebraic value of E^0 than has the corresponding element in the next higher group.
6. In the A family of Group V and in the A family of Group VI, E^0 decreases in algebraic value with an increase in atomic number. Uranium is an exception.
7. In the B family of Group VI and in the B family of Group VII, E^0 increases in algebraic value with an increase in atomic number.
8. In Group VIII E^0 decreases in algebraic value with an increase in atomic number, with the exception of the Pd–Os sequence.

It should be noted that the relationships between the relative reactivities of organo-metallic compounds of the elements and their positions in the periodic table, as formulated by Gilman,[4] are identical with those existing between the algebraic values of E^0 of the elements and their positions in the periodic table as set forth in Rules 3 to 7 inclusive.

[1] PALMAER, "Nernst's Festschrift," Knapp, Halle, **1912**, p. 332.
[2] THOMLINSON, *Chem. News*, **117**, 176 (1918).
[3] LATIMER, "Oxidation states of the elements and their potentials in aqueous solutions," Prentice-Hall, Inc., New York City, **1938**.
[4] GILMAN, "Organic chemistry: an advanced treatise," John Wiley and Sons, Inc., New York City, **1938**, Vol. I, p. 436.

Heavy Water

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IF A direct current of electricity is passed through water, the water is decomposed into its elements, hydrogen and oxygen. Pure water is not a very good conductor of electricity, but its conductance may be very greatly improved by adding to it a little sulfuric acid or a little sodium hydroxide, that is, ordinary lye.

Water is such a common substance and has been studied in scientific laboratories so thoroughly that most people felt up until 1933 that there was little more to learn about water or about the way it was decomposed by electricity. But that year two of the country's leading scientists, Professor Harold C. Urey of Columbia University and the late Dr. Edward W. Washburn of the Bureau of Standards in Washington, D. C., made a very remarkable discovery. They discovered that when water is being electrolyzed, the water remaining in the container keeps getting heavier. Instead of weighing 62 pounds per gallon as does ordinary water, this residue of water in the container gradually increases in specific gravity until ultimately it weighs over 68 pounds per gallon. This material is just as much entitled to the name "water" as is the ordinary water we drink, yet it differs in many ways. It was promptly named "heavy water."

Experiments soon showed that it was the hydrogen that gave the "heaviness" to heavy water. The way this was proved was as follows. A sample of heavy water was decomposed into hydrogen and oxygen. The hydrogen was then combined again with ordinary oxygen and the water so formed was found to be heavy water. But when the oxygen from the original sample of heavy water was combined with ordinary hydrogen, only ordinary water resulted. It was clear, therefore, that it was the hydrogen that contributed to the peculiar properties of heavy water.

The hydrogen atoms in heavy water weigh twice as much as the hydrogen atoms in ordinary water. Atoms of the same chemical element but of different weights are called "isotopes." "Heavy" hydrogen is, therefore, an isotope of hydrogen. This substance was discovered in 1931 by Professor Urey, who was awarded the Nobel Prize for his work. Generally the different isotopes of an element are not given special names, but the properties of heavy hydrogen are so unique that Professor Urey named it "deuterium," with the symbol D. Heavy water, therefore, becomes D_2O instead of H_2O which is, of course, the chemical formula for ordinary water. Deuterium is not regarded as a new chemical element, but its discovery was even more important than the discovery of some elements, because deuterium at once proved to be such a useful research tool in the scientific laboratory.

The preparation of pure D_2O is an expensive and tedious job. In the first place there is only a single cupful of heavy water in nearly four hundred gallons of ordinary water. And then it has not so far proved possible to extract the heavy water without losing much of it in the process. In one plant it was found that less than an ounce of heavy water could be obtained from a ton of ordinary water. A very large amount of electricity is necessary to decompose so much water, and so far it has not been possible to produce heavy water for much less than $15 per ounce. Searches have been made for richer sources of heavy water, and some Russian scientists have found that water from deep in the bowels of the earth is slightly richer in D_2O. But the difference is so slight that it can make little or no difference in the cost of the product. Patents have been granted in the United States and in other countries for several processes for concentrating heavy water.

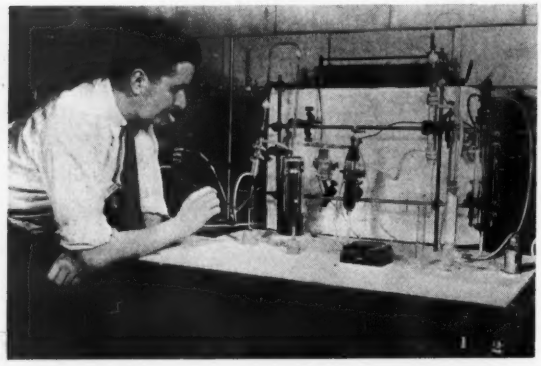
Photograph by Bachrach

PROFESSOR HAROLD C. UREY, DISCOVERER OF HEAVY HYDROGEN

It is clear that a container large enough to hold, say, 400 gallons of tap water, would scarcely be moistened inside by the cupful of heavy water finally obtained. For this reason it is customary to work in several successive stages using progressively smaller or fewer containers. Table 1 shows how the heavy water was gradually enriched in a process which involved seven stages.

It should be mentioned that it is possible to prepare pure "light" water too. If the gases coming off during

the electrolysis of tap water are caught and recombined, the water so formed will be found to contain little or no deuterium. The reason for this is, of course, that most of the deuterium remains behind in the electrolysis



THE AUTHOR, WITH APPARATUS USED AT PRINCETON UNIVERSITY DURING THE FINAL PURIFICATION OF HEAVY WATER

cell. But such pure light water differs only very slightly indeed from tap water.

TABLE 1

Stage of Electrolysis	*Per Cent Heavy Hydrogen*	*Volume Electrolyzed*
1	....	610 gal.
2	0.5	90 gal.
3	2.5	12.5 gal.
4	8	2.5 gal.
5	30	2 quarts
6	93	1 pint
7	99	3 ounces

It is also possible to make "half-heavy" water, or water whose formula is HDO. If this is obtained as steam, it may be kept and studied, but the moment it turns into liquid water it becomes a mixture of H_2O, HDO, and D_2O.

Heavy water differs in many ways from ordinary water. To be sure, it looks, smells, and tastes like ordinary water, but it is about 10 per cent heavier, or to be exact, its specific gravity is 1.1078 times that of ordinary water. This difference in specific gravity is the easiest way to identify heavy water or to tell what amount of heavy water may be present mixed with ordinary water. Some very sensitive methods have been worked out for measuring very slight changes in specific gravity, and it is possible by this means to detect as little as one part in 1,000,000 of heavy water. One of the ways of doing this is to make a little glass float of such weight that it will neither rise nor fall if placed in a tube full of ordinary water. Then if the float is placed in heavy water it will promptly rise to the surface because the heavy water buoys it up.

Heavy water boils at 214.6°F. instead of 212°, and it freezes at 38.9°F. instead of 32°. It is noticeably more viscous, that is, more sirupy than ordinary water; and it is not possible to dissolve quite so much salt in heavy water as in ordinary water.

One of the first things tried when heavy water was discovered was to see what effect it would have on living organisms. The first sample of practically pure heavy water was obtained by Professor Gilbert N. Lewis of the University of California. Professor Lewis soon found that the germination of tobacco seeds was restrained or entirely stopped in heavy water, although he had scarcely more than a drop of water to work with.

Other experimenters found that nearly pure heavy water killed tadpoles, worms, or small fish, but 32 per cent heavy water did not have any effect on them. Heavy water is not poisonous in the sense that carbolic acid is a poison, and to certain bacteria it seems scarcely to be harmful at all. At one time it was suggested that old age and senile decay were caused by accumulation of heavy water in the body, but that theory was soon shown to be quite false. Heavy water is not poisonous, but it is generally unfavorable to the growth and health of living organisms, and at least the more complex organisms such as mice soon die when given nothing but heavy water to drink.

It is a strange fact that when mice or rats are given heavy water to drink they become very thirsty. Why this should be so is not clear, but the molecules of heavy water, in addition to being heavier, move more slowly than the molecules of ordinary water. When water moves into living cells it does so by the process known as osmosis, and the rate of osmosis of heavy water is considerably slower than for ordinary water. Perhaps this accounts for the thirst reaction of mice and rats. At any rate, nearly all biological processes are slower in heavy water. If a football coach wanted to increase the weight of his line, he might, in theory at least, make all the players drink heavy water. But the increase in weight would be at the expense of the speed of movement and probably of mental alertness too.

If care is taken, heavy water may be fed to mice for a long time, and when that is done their growth is slowed down. In some types of organisms not only the growth but the onset of old age is slowed down also. It may be, therefore, that life could be prolonged and old age postponed awhile by drinking a tumblerful of heavy water every day. But the extra life would only be gained at the expense of alertness. The chances of getting run over by an automobile would be just that much increased.

Everyone knows that the body is made up largely of water. Mice have been fed heavy water until its concentration reached 20 per cent of all the body water, without serious ill effects. This may be achieved by giving the mice nothing but heavy water to drink for two days. But if the concentration of heavy water in the body reaches 40 per cent, the mice soon die and degeneration of the liver and spleen is found to have occurred. As a matter of fact some pathological changes begin to take place even at much lower concentrations of heavy water.

The possibility of using heavy water in the treatment of cancer has been investigated. Although the growth of cancers in mice is slowed down slightly by giving the mice heavy water, yet this is not regarded at the present time as giving any hope for eventual cure of the disease.

Some of the research centered around heavy water has been concerned with deuterium itself rather than with D_2O. Heavy hydrogen, or deuterium, has the formula D_2 and is a gas similar to hydrogen except that it is twice as heavy. For research purposes, pure deuterium gas is prepared by passing an electric current through pure heavy water to which a small amount of sodium hydroxide is added to increase the electrical conductivity. Of course, it would not do to add ordinary sodium hydroxide, NaOH, because this would introduce some ordinary hydrogen. What must be added is some heavy sodium hydroxide, NaOD. This substance can easily be prepared during the concentration of heavy water.

It often happens that very small amounts of heavy hydrogen must be detected and accurately analyzed. This is done by means of an instrument called a Pirani gage. If a fine platinum wire is connected to a storage battery, the wire will warm up and even glow like the filament in an electric light bulb. The electric current necessary to warm the wire to a given temperature depends not only on the size of the wire but also on how rapidly the wire is cooled by the atmosphere that surrounds it. It happens that ordinary hydrogen conducts heat away from the wire, cooling it considerably faster than heavy hydrogen. Consequently the amount of deuterium in a sample of hydrogen may easily be found by determining the electric current necessary to keep the platinum wire at a definite temperature.

When deuterium was discovered scientists began to wonder if there might not be a third isotope of hydrogen and a "superheavy" water. At one time it was believed that the third isotope had been found in ordinary tap water, but there is some doubt about this at the present time. However, it has definitely been possible to make the third isotope synthetically, although always in extremely small amounts. The isotope made synthetically is radioactive, but this is not true of deuterium. This third isotope of hydrogen is called "tritium," with the symbol T. There is, therefore, a possible T_2O. As a matter of fact there is no reason, at least in theory, why we should not also have HTO, and DTO, although no one has yet been able to obtain enough tritium to study the waters which might be made from it. But, in theory, there are six possible kinds of water, H_2O, HDO, D_2O, HTO, DTO, and T_2O.

Oxygen also has isotopes although less success has been had in separating these than in the case of deuterium. These oxygen isotopes are much more nearly alike than are hydrogen and deuterium. If the atomic weight of the commonest oxygen isotope is taken as 16, then the other two are 17 and 18, respectively. They do not have special names, but their chemical symbols are written O^{16}, O^{17}, and O^{18}, respectively. Electrolysis does not prove to be a practical method for separating these isotopes, but Professor Urey has succeeded in separating small quantities of the nearly pure isotopes by other means. One of the most interesting things about the oxygen isotopes is that they raise to eighteen the total number of different kinds of water theoretically possible. These are

H_2O^{16}	H_2O^{17}	H_2O^{18}
HDO^{16}	HDO^{17}	HDO^{18}
HTO^{16}	HTO^{17}	HTO^{18}
D_2O^{16}	D_2O^{17}	D_2O^{18}
DTO^{16}	DTO^{17}	DTO^{18}
T_2O^{16}	T_2O^{17}	T_2O^{18}

Most of these have not and perhaps may never be prepared pure. But someone has estimated that the heaviest kind of heavy water, T_2O^{18}, would have a specific gravity of 1.33, a boiling point of nearly 217°F., and a freezing point of about 50°F. It would freeze on any moderately cool day. Commercial heavy water obtained from Norway contains 0.32 per cent of D_2O^{18}.

Hydrogen is found in many chemical compounds besides water, and there is no reason why deuterium could not be used in these compounds instead of hydrogen. For instance, heavy sulfuric acid has been made by dissolving sulfur trioxide in heavy water instead of in ordinary water.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
$$SO_3 + D_2O \longrightarrow D_2SO_4$$

In similar fashion a great many compounds containing deuterium have been prepared. A few of these are DCl, DBr, DI, D_2S, ND_3, ND_4Cl, all of which will be recognized by any student of chemistry. Organic compounds may also be prepared containing one or more deuterium atoms in the molecule. Benzene, C_6H_6, may be converted to a whole series of substances C_6H_5D, $C_6H_4D_2$, $C_6H_3D_3$, $C_6H_2D_4$, C_6HD_5, and C_6D_6. The last is sometimes called hexadeuterobenzene. Heavy sugar would be $C_{12}D_{22}O_{11}$, heavy alcohol C_2D_5OD. All these compounds resemble the ordinary compounds containing hydrogen. The differences in weight and in other properties depend on how much deuterium is present. In one or two cases the deuterium compounds are slightly colored while the corresponding hydrogen compounds are colorless.

The principal uses of deuterium and of heavy water are as indicators in what are called "exchange" reactions. The meaning of the word "indicator" may be illustrated as follows: Suppose on a pitch dark night one heard squadrons of airplanes flying overhead. Without the aid of searchlights, efforts to hit one of the planes with an anti-aircraft gun would be practically useless. But if even a single plane in each squadron carried a light, the problem of finding the squadrons would be immeasurably simplified. Just as the single plane with a light would be an indicator for the movements of the whole squadron, so a few deuterium atoms may indicate the course of countless hydrogen atoms in a chemical reaction.

Every student of chemistry knows that even a single drop of water contains about 100,000,000,000,000,000,000 molecules. This vast number is illustrated by the following imaginary experiment which may be found described in almost any elementary textbook of chemistry. Suppose a glass full of water were to be

taken from the ocean and each molecule in it carefully marked with a red label. Then suppose the water to be thrown out into the ocean again, and time allowed for that glassful of water to become completely mixed with all the water in all the oceans, lakes, and rivers on the earth. Then take once more a glass full of water from the ocean, and you will find over a thousand red-labeled water molecules in the glass.

Of course this experiment has always been called imaginary, because it would be impossible to label a single molecule, not to mention the countless billions which would be found in a tumblerful of water. But the experiment is no longer imaginary. Molecules of heavy water are labeled by nature, and may always be recognized by their heaviness. Anyone who cared to go to the trouble could do the experiment by using a glassful of heavy water instead of the imaginary red-labeled molecules.

Suppose hydrogen chloride, HCl, is dissolved in water, then pumped off again. Is the hydrogen atom that goes into solution the same one that comes out, or does the hydrogen in hydrogen chloride perhaps change places with one of the hydrogens in the water? If we dissolve ammonia, NH_3, in water, do the hydrogen atoms in the ammonia change places with one or both of those in water? If we drink a glassful of water, are some of the hydrogen atoms in the water built into the fats and proteins of our bodies, or are they all eliminated again just as they were taken in? These and many similar questions are answered by experiments with heavy water.

Experiments show that in the case of HCl, of NH_3, and of many other substances, the hydrogen atoms are exchanged back and forth instantly when the substances are dissolved in heavy water

$$HCl + D_2O \longrightarrow DCl + HDO$$

But if hydrogen gas is dissolved in heavy water, no exchange takes place unless the mixture is heated for several hours with a little sodium hydroxide, or if some platinum black or other "activating" agent is present. Apparently in hydrogen gas the two hydrogen atoms are held together much more tightly than is, say, hydrogen to chlorine in HCl,

$$H_2 + D_2O \longrightarrow \text{no exchange}$$
$$HCl + D_2O \longrightarrow \text{rapid exchange}$$

In the case of sugar, $C_{12}H_{22}O_{11}$, half the hydrogen atoms are exchanged very rapidly, but the others not at all, proving what chemists have long suspected, that half the hydrogen atoms in sugar are attached in a different way from the rest.

The hydrogen atoms in hydrogen sulfide, H_2S, are readily exchanged, but those in methane, CH_4, are not. In hydrogen peroxide, H_2O_2, both hydrogens are easily exchanged, but in carbolic acid, C_6H_5OH, and in benzoic acid, C_6H_5COOH, only one hydrogen atom is exchanged in each, although each compound has five other hydrogen atoms in the molecule. In fact it has been found that wherever hydrogen is attached to oxygen, nitrogen, sulfur, fluorine, chlorine, bromine, or iodine, it is easily exchanged; but where hydrogen is attached to carbon it is often exchanged only with great difficulty. Experiments such as these, even though they may at the time have only theoretical interest, add to our general knowledge of the structure of matter and may in time lead to important practical advances.

The simplest exchange reaction of all is that of hydrogen with deuterium

$$H_2 + D_2 \longrightarrow 2HD$$

to yield "half-heavy" hydrogen. This exchange does not take place under ordinary conditions. However, in chemistry there are many examples of substances which, while not themselves being altered, nevertheless speed up to a remarkable degree certain types of reactions. Substances which speed up chemical reactions are called "catalysts," and many if not most chemical industries are dependent on catalysts for their very existence. In fact few branches of chemistry are of more practical significance than is the study of catalysts. For instance, the manufacture of sulfuric acid, ammonia (for fertilizers and explosives), alcohol, edible fat substitutes, aviation gasoline, and plastics simply would not exist if it were not for the catalysts which make them commercial successes. There have been found catalysts which accelerate the exchange reaction of hydrogen and deuterium. One of these catalysts is nickel and another is chromium oxide. Professor Hugh S. Taylor of Princeton University made the discovery that chromium oxide will catalyze the hydrogen-deuterium exchange reaction even at nearly 200°F. below zero.

This result is of real industrial significance. In many industrial catalytic reactions, such as the synthesis of ammonia, it is still necessary to work at high, and hence expensive, temperatures, even though efficient catalysts are used. Furthermore, the very use of high temperatures often cuts down the yield of product. Professor Taylor's experiments show that it is not the hydrogen which requires such a high temperature for its reaction, because the hydrogen will react with deuterium on chromium oxide at extremes of cold. If catalysts could be found as active toward other molecules as chromium oxide is to hydrogen, tremendous improvements in the yields of products such as ammonia and industrial alcohol could be made. Not only would the yields be greater, but the products would be cheaper and would be made under much simpler, and in some cases less hazardous, operating conditions. The experiments with deuterium show a definite direction which research in industrial catalysis must take.

Some of the most important applications of heavy water have to do with its use as an indicator in physiological processes, that is, in the chemical changes taking place in the human or animal body. It is well known that the body consists in large part of water, and the question might arise: When a person drinks a glass of water, are the hydrogen atoms in that water distributed throughout the whole body or are they eliminated at once? Are the hydrogen atoms in the

tissues of the body being continually replaced by other hydrogen atoms, or are the body tissues simply washed by the water which is then quickly excreted? Before heavy water was discovered there was no way to approach these problems.

Professor George von Hevesy, in Germany, found that goldfish put in dilute heavy water quickly absorbed the heavy water until the concentration of heavy water was about the same inside the fish and out. The total concentration of heavy water was so low that the fish did not suffer any ill effects from this experiment. The speed of exchange is so great that in a few hours no further concentration of heavy water in the fish can be detected, although the speed of exchange is less with larger fish. Even in dead fish there is an unmistakable although slower exchange. If the fish, now containing heavy water, is put back in ordinary tap water, the heavy water quickly diffuses back out of the fish again. This experiment shows that, at least so far as fishes are concerned, water can diffuse back and forth throughout the whole body without the fish being in any way aware of what is going on.

The next question is: How long does the average water molecule stay in the human body? Professor von Hevesy has answered this question too. A man drank two quarts of water containing about one-half per cent D_2O. Heavy water began to appear in the urine only 26 minutes later, but it was not completely eliminated for many days. Taking into consideration all the heavy water eliminated, in urine, through perspiration, and through the lungs, it took about 9 to 10 days for half of the heavy water, and therefore half of the two-quart test drink, to be eliminated. This does not, of course, mean that the man excreted only one quart of water in 10 days, but that it took 10 days to eliminate half the number of actual molecules of water swallowed at the beginning of the experiment. On the average a water molecule stays in the body about 14 days before being eliminated. This is especially interesting, because if a person drinks a substance such as methylene blue, the urine is soon strongly colored blue, but the color all disappears, that is, the methylene blue is all eliminated from the body within 43 hours. These experiments show that water swallowed diffuses throughout the whole body and becomes part of the animal tissues before being slowly eliminated. A few hydrogen atoms probably manage to stay in the body many months if not years.

One of the most successful applications of deuterium has been carried out by Professor David Rittenberg and his associates at the College of Physicians and Surgeons of Columbia University. These scientists have been mostly interested in animal metabolism, that is, the process by which the foods we eat are used to repair tissues and supply energy for our bodies. Metabolism studies are useful to physicians and to the public alike because few things are of more importance to human health than what we eat.

One of the greatest stumbling blocks in the study of metabolism has been that the foods eaten are often exactly the same as substances which are continually being synthesized and destroyed in the animal body. If substances such as natural fatty acids (found in fats, butter, lards, etc.), or amino acids (found in meat), are administered to an animal, we lose track of them the moment they enter the body, since they are mixed with the same substances already present. Fortunately the discovery of deuterium offers almost unlimited opportunity for studying the transportation of organic molecules in the body. In many cases it is also useful for investigating the conversion of one substance into another.

Animals use fat largely for producing energy. They do this by a process exactly equivalent to burning the fat to make a steam engine go. However, whenever an excess of fat presents itself in the diet, the animal stores it up in certain locations in the body called "fat depots." The first question Professor Rittenberg asked was this: When animals are fed a diet somewhat deficient in fats, do they use the fat they get directly or do they still store it in the fat depots and then use it as most urgently required? In order to answer this question he prepared some stearic acid (found in lard) which had a few deuterium atoms in the molecule. These deuterium atoms acted as a label to tell what happened to the stearic acid. The labeled stearic acid was made by taking linoleic acid (found in linseed oil) and treating it with deuterium in the presence of a catalyst. The reaction is represented by the equation:

$$\underset{\text{linoleic acid}}{C_{17}H_{31}COOH} + \underset{\text{deuterium}}{2D_2} \longrightarrow \underset{\text{labeled stearic acid}}{C_{17}H_{31}D_4COOH}$$

Ordinary stearic acid is $C_{17}H_{35}COOH$. Mice were fed this labeled stearic acid, then the mice were killed and examined to see if the fatty acid had been used up directly or if it had been deposited, as indicated by the presence of deuterium atoms in the fat depots. Most of the deuterium was found in the fat depots, proving that even when the diet is deficient in fats, most of the fat is stored up before being used.

Another investigation carried on by Professor Rittenberg concerns butyric acid, found in butter fat. Although butyric acid is always present in a normal diet it is never found in the fat depots of the body. The question arises: Is the butyric acid used up directly or is it first converted into another fatty acid and then stored?

In order to answer this question mice were fed butyric acid containing deuterium atoms, but almost no deuterium was afterward found in the fat depots. All the deuterium was quickly excreted. But this experiment does not prove what happened to the butyric acid. The deuterium might, to be sure, have been liberated when the butyric acid was burned up in the body, or it might have been lost when the butyric acid molecules were converted into some other fatty acid for storage. The deuterium is, after all, only a label, and it is possible for the label to be lost from a molecule just as the label on a trunk might be lost in an express office.

In order to solve this problem, heavy water was in-

jected into mice until the concentration of deuterium atoms reached three per cent. The mice were then fed *ordinary* butyric acid. The idea was that if the butyric acid were converted into some other fatty acid in the body, the conversion would be taking place in the presence of dilute heavy water, and the new fatty acid would in all probability contain some deuterium atoms. But when this was done, still no deuterium was found in the stored fats. In the body butyric acid is, therefore, burned directly and is not stored in any way. Butyric acid is not a fat former, in the ordinary sense. This does not mean that butter will not make a person fat. The butyric acid may supply all the energy requirements leaving other fats to be stored.

Many similar types of investigations have been and are being carried on in the scientific research laboratories of the world, and it is interesting to know that the discovery and many of the applications of heavy hydrogen were made in the laboratories of the great universities of this nation.

TEACHING WEIGHING TECHNIC WITH THE AID OF A MOTION PICTURE FILM[1]

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THE usual method of instruction employed to teach analytical balance technic in the first course in quantitative chemical analysis is to divide the class of students into small groups of four or five who gather around the balance to watch the instructor demonstrate the accepted methods of handling the balance controls and the other necessary operations. This procedure must be repeated several times until the entire class has seen the demonstration. Discussion and illustration of the method of calculating the final weight of the sample is usually reserved until a later time when the entire class is assembled. In using this time-honored and time-consuming method the student does not have adequate opportunity to see the detailed technic of weighing and he does not have presented to him the whole process of weighing and calculation of the final weight of the sample.

With the triple objectives of (1) shortening the time required for students adequately to absorb weighing fundamentals, (2) increasing the effectiveness of teaching balance technic, and (3) making the study of quantitative analysis more interesting for the student, we have produced a motion picture film incorporating all essential details of the weighing procedure. The film has already been used and tested with two of our regular classes in quantitative analysis and has proved to be far superior to the usual method of instruction.

The film, contained on two 400-foot reels, is of the silent 16-mm. type, 531 feet in length. An unusual feature is the provision for brief pauses to allow for calculations to be made on the board by the instructor. This is accomplished by the use of "STOP" titles spliced into the reel at appropriate points. The operator is instructed to watch for these "STOP" titles, and to stop the projector for a few minutes at each one of them so that the lights may be turned on in the room and the instructor may make a calculation on the blackboard. For instance, immediately after a "rest point," "sensitivity," or "final weight" has been demonstrated on the film, the instructor records the results in tabular form on the blackboard and, at the proper place and time, demonstrates on the blackboard how the final weights are calculated. In this manner the student is given an integrated demonstration of weighing operations and the methods of calculation of the final weights by the sensitivity method.

The technic of using this type of film as a teaching aid is of course most important. We have found the following procedure to be most effective and believe that it could be successfully employed with either small or large classes:

First Meeting of the Class.—This consists of a discussion of the theory of weighing (rest points, sensitivity, etc.) and analytical balance construction and characteristics, and also an examination of sets of analytical weights. Just prior to this period the class has been assigned the chapter in the text dealing with the subject of weighing. The method of weighing by sensitivity is thoroughly discussed.

Second Meeting of the Class.—At this meeting a lecture demonstration, employing the film described, is given by the instructor. As noted, the projection of the film is stopped at appropriate intervals and blackboard calculations of rest points, sensitivities, and final weights are made by the instructor. At these "stop" intervals, opportunity is also given for questions from the class. The film progressively illustrates the following technics: preparation of the balance before weighing; handling of the balance controls; determination of rest points and sensitivities; actual weighing of (1) a simple metal object, (2) tare of watch crystals, and (3) a powdered ore sample. When the showing of the film has been completed the class has seen the weighing of three separate objects and the complete calculation of their final weights. During the entire time that the film is being shown the instructor stands near the screen with a pointer and calls attention to those technics that require emphasis.

Since we have found this film to be entirely satisfactory as a substitute for the traditional method of instruction it may be that others would like to use it. Correspondence with the author is invited.

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Alexander Borodin—Musician and Chemist

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IT IS not unusual for men of science to follow hobbies wholly unrelated to their professions. Rarely, however, do these hobbies become so all-absorbing as to cause a complete change in the careers of those who indulge in them. Yet such was the case with Borodin, chemist and teacher, known to us as the composer of *Prince Igor* and other musical works of the first magnitude.

From the musician's point of view, Borodin was not unique in the division of his efforts between two loves. He was but following the excellent tradition set by others of the small group of "neo-Russians," who in the latter half of the nineteenth century set out to re-create Russian music on the basis of national folk song. Among these, Cui was a Lieutenant-General of Engineers and professor of fortification; Rimsky-Korsakov, a naval officer; Moussorgsky, a member of the army; Serov, a graduate of the school of jurisprudence; Glinka, a clerk in the Ministry of Ways and Means; and Balakirev debated whether to take up mathematics professionally and keep music as a side line. Tschaikowsky was also a member of this school of musicians, but he remained aloof from the little group.

It has been said (*5*) that Borodin had the smallest output with the highest average of excellence of any composer in history. He was first known outside of Russia for his tone-poem *In the Steppes of Central Asia*. Music with him was a means of amusement; he composed *Prince Igor* when he was too ill to do anything else.

A discussion of Borodin's musical career or its critical evaluation is out of place here; it is the object of this account to describe a lesser known side—the man as a chemist, some of whose unfamiliar contributions to this science have been collected from scattered sources and tabulated here. Yet the two sides of his nature were so intimately bound together that it is not always possible to separate them. It is almost necessary to treat them as parallels.

Alexander Borodin was the illegitimate son of Prince Luke Ghedeanof of Imeretia, a descendant of Caucasian nobility, and Eudoxia Kleineke, a woman of the middle classes. For the sake of propriety he was registered as the son of one of his father's serfs, Porphyri Borodin, whose name was given to the child. His mother was a cultured and intelligent woman, who taught the child with tender care. As a small boy he began to show more than a casual interest in music and the natural sciences. He began his informal musical studies and at the same time he eagerly studied chemistry. He fitted up a laboratory in his own room and spent much time performing experiments and making fireworks. He frequently entertained friends by conjuring strange tricks through the medium of chemistry. As if this were not enough for one young boy, he added to his hobbies those of modeling and painting, using pigments which he made himself.

In 1850, at the age of sixteen, he matriculated at the Academy of Medicine and Surgery at St. Petersburg,

ALEXANDER BORODIN (1834–87)

Russian musical composer and chemist; one of the founders of a school of medicine for women in Russia

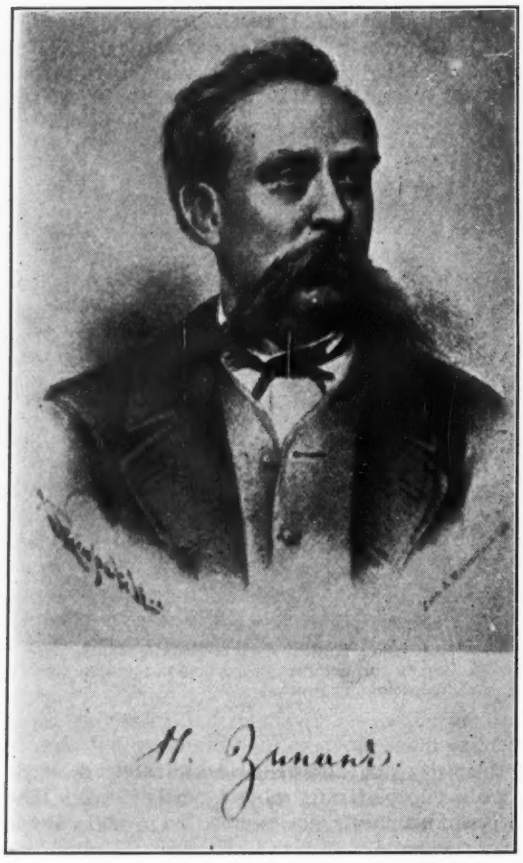
where he made progress in all branches, but especially in chemistry and botany. He ultimately decided to specialize in the former subject, partly through the influence of his master, the chemist Zinin, whom Borodin greatly admired.

With ever-increasing intensity he devoted himself to his two loves, music and chemistry. His strenuous effort to serve two masters probably accounts for his early death. "Mr. Borodin," Zinin used to say to him (*1*), "please do not think so much of ballads, when here I am believing in your future and trying to train you to succeed me. You cannot hunt two hares at the same time."

But Borodin did hunt both hares successfully. He improved his knowledge of musical forms and composed several of his early works. Year after year he shone in his musical studies at the Academy, and passed all his academic examinations with distinction. In 1856 he was appointed assistant to the professor of pathology and therapeutics. Shortly before presenting his thesis to the Academy, he was sent to attend a medical conference in Brussels, where he was later to score his first noteworthy musical successes outside Russia. His thesis, "The Analogies between Arsenious Acid and Phosphorous Acid," compared the two acids from a chemical and toxicological point of view, and

won him the degree of Doctor of Medicine in May, 1858.

Previously he had some experience as physician in a military hospital. His work there—dressing wounds for serfs who had been cruelly beaten—greatly affected



NIKOLAĬ NIKOLAEVICH ZININ (1812–80)

Russian organic chemist; occupied the chair of chemistry at the University of Kazan and later at the Medico-Surgical Academy of St. Petersburg; was Borodin's professor and constant source of inspiration; prepared aniline by reduction of nitrobenzene

his sensitive nature, and decided for him finally that rather than remain a practicing physician, he would devote himself entirely to research.

Throughout the remainder of his life the two activities continued to take parallel courses. Years were to elapse before he actually came to the front as a composer. In 1859 he went abroad at the government's expense to continue his scientific studies. He spent a winter at Heidelberg working under Kekulé and Erlenmeyer, and the following summer in Italy and Switzerland. Finally he paid a short visit to Paris before returning to Heidelberg. On two occasions he had as roommate, and also as traveling companion while in Italy, the illustrious Siberian chemist, Mendeleeff. He traveled in France also and met Wurtz, another of the great chemists of that day. During these and the following years, he published eight papers on chemical subjects in Russian, French, and Italian journals. Shortly before his twenty-ninth birthday he returned to St. Petersburg, having shown much promise as a scientist, but still an amateur as a composer. As for the latter, most of the technic he had acquired was self-taught. It was Balakirev who was the first to tell Borodin that composition should become his real calling.

In December, 1862, he was appointed assistant professor of organic chemistry at the Academy, and in 1864 rose to the rank of professor. He was always popular as a teacher, being noted for his cheerfulness, thoughtfulness, knowledge, kindness, and enthusiasm for helping. His marriage—a very happy one—took place in 1863 to Catherine Protopopova, a young pianist whom he met while in Heidelberg.

One of his students, who afterward became a professor at the same Academy, wrote:

> "When working in his laboratory, we felt as if we were in our own home. Even while at work he never forgot music. He would hum tunes, talk with us of his new works, technic, or tendencies. And after he had withdrawn to his private flat, we often heard the sound of the professorial piano."

Borodin's researches (*3*) at this time (1862) led him to the conclusion that the fluorides of organic radicals are more like their chlorides than the fluorides of metals are like the corresponding metallic chlorides. He was the first to prepare benzoyl fluoride, and he studied the action of zinc ethyl on chloro-iodoform. Yet his main general subject was the properties of aldehydes, a study which led to many bypaths and ramifications. By condensation of two molecules of acetaldehyde, he discovered aldol simultaneously with Wurtz (1872). A similar reaction—the "aldol condensation"—applied to the formation of many other compounds.

He studied the action of sodium on valeraldehyde and so was led to the investigation of capric and isocapric acids. By the action of hydrochloric acid on ordinary acetaldehyde he obtained an aldol, which on oxidation gave β-oxy-butyric acid. Being familiar with these aliphatic aldehyde reactions, he went over into the field of aromatic aldehydes. For instance, he studied the action of ammonia on benzaldehyde to form hydrobenzamide. By simple heating, he accomplished the transformation of the hydrobenzamide into amarine, whose composition he studied, along with that of hydrobenzamide. He was able to throw light on the structure of both these compounds.

If we neglect the musical side of the next years, which were fruitful in producing the beginnings of his opera *Prince Igor* and his first and second symphonies, his scientific and educational activities were manifold. Along with Madame Tarnovskaya and Professor Rudnev, Borodin played an important part in founding a School of Medicine for Women in St. Petersburg, and took charge of some of the courses in chemistry in addition to his other duties. In these courses he continued to be principal lecturer for some fifteen years, until his

death. He was deluged with meetings and important academic conferences.

He organized his own laboratory on a new basis, making it available for students and paying all the expenses himself. This left him little time for music. Borodin once wrote to a friend (*2*):

"In winter, I can only compose when I am too unwell to give my lectures. So my friends, reversing the usual custom, never say to me 'I hope you are well,' but 'I hope you are ill.'"

At another time he wrote,

"I am almost ashamed to confess my composing activity. Others have the composition of music . . . the goal of their lives. For me, it is only rest, fun which takes time from my serious business as a professor. I am absorbed in my affairs, my science, my academy, and my students. Men and women students are dear to me."

In 1877, with two of his pupils, he visited the laboratories of the important universities in Germany, with Weimar as the principal goal,[1] having in mind the reorganization of the chemical section of the Petersburg Academy. From 1880 to 1886—the year in which his last scientific paper appeared—his time, when he was not ill, was largely given over to music. His last paper concerned the determination of nitrogen and its transformations in the organism. His researches were generally successful; one of the last works in which he engaged was the development of a method of determining nitrogen metabolism, published in 1886.

Characteristic of the feverish activity in which he lived was the manner of his death, on February 28, 1887. After spending a busy day working on his third symphony, Borodin attended a dance given by the professors of the Academy. He was dressed in Russian national costume, and was strikingly handsome after the Oriental manner of his father. He was said to have been in high spirits. In the midst of the festivities, while conversing gaily with the guests, he collapsed and died a brief moment later without a sigh.

He is buried in the Alexander Nevsky cemetery, close by the tombs of Moussorgsky, Glinka, Balakirev, Dostoyevsky, Tschaikowsky, and Rubinstein. Themes from his greatest musical works and formulas of chemical substances which he studied are engraved on his monument, which was placed over his grave two years after his death. His former students placed a wreath on his monument with the inscription (*6*):

"To the founder, defender, and guardian of the medical classes for women, to the friend of pupils—from women physicians of ten classes."

Sarton, the historian of science, sums up Borodin's worth as follows (*8*):

"The chemical fame of Borodin is not comparable with that of Zinin—who was one of the most distinguished leaders of Russian science and who obtained international recognition. Borodin's fame is humbler, but none the less important. His best has been assimilated into the growing chemical knowledge of the last century. Borodin did not make any outstanding discovery; he was nevertheless a distinguished chemist."

Comparing the chemist with the musician, he continues,

"The chemist Borodin will never be more than a shadowy figure except to the very few men who happen to use his papers and walk in his footsteps, while the musician Borodin is a dear old friend to thousands of people all over the world."

It is interesting to note that the Soviet Government, recently dedicating a monument to Borodin, honored him not for his music but for his medical services to the Russian people. It has been said of him:

"No musician has ever claimed immortality with so slender an offering. Yet if there be, indeed, immortalities in music, his claim is incontestable."

[1] The visit to Weimar was musical as well as chemical in its significance (*4*). "Liszt was once more there, and his court and school are described by Borodin in the series of delightful letters to his wife, afterwards published by his friend and biographer, Vladimir Stassov. These letters present an incomparable portrait of the great virtuoso, and reveal his intimate views upon the music of the new Russian school."

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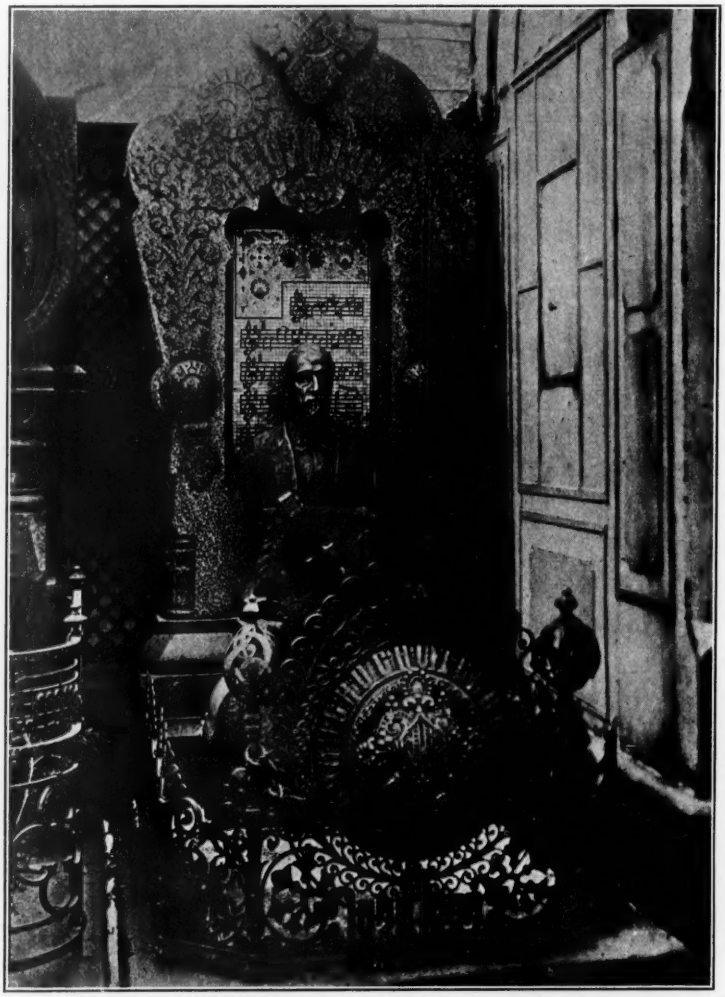

MONUMENT OVER THE GRAVE OF BORODIN, BEARING THEMES FROM HIS GREATEST MUSICAL COMPOSITIONS AND FORMULAS OF SOME OF THE CHEMICAL SUBSTANCES HE STUDIED

MUSICAL WORKS OF BORODIN

First Symphony in E flat major (1862–7).

Four Songs (Jurgenson, Moscow).

Four Songs (Bessel and Company, St. Petersburg).

First String Quartet, in A major, on a theme from the finale of Beethoven's quartet, page 130 (finished 1878).

Second Symphony in B minor (1871–7).

The Paraphrases, twenty-four variations and fourteen pieces for piano, "on a favorite theme" (that is, the childish tune known in Germany as the "Coteletten Polka," and in England as the "Chopsticks Waltz"). The Polka, Marche Funèbre, and Requiem are by Borodin—the other members of the new Russian school, and Liszt, being among the contributors.

In the Steppes of Central Asia. Symphonic Sketch (1880).

Petite Suite for Pianoforte, dedicated to Countess Mercy Argenteau (1885).

Scherzo in A flat major, for orchestra.

Septains: verses for pianoforte and voice, dedicated to Countess Mercy Argenteau (1886).

Quartet on the name B-la-f (Belaieff), by Borodin, Rimsky-Korsakov, Liadov, and Glazounov.

Serenata espagnola, for the pianoforte (four hands).

Posthumous Works

Second Quartet, in D major.
Prince Igor: opera in four acts with a prologue.
Arab Melody, for voice and piano.
Song to words by Pushkin (Composed in 1881 on the death of Moussorgsky).
Sérénade de quatre galants à une dame. Humorous quartet for male voices.
Song, words translated from Count A. Tolstoi: "La Vanité marche en se gonflant."
"Chez ceux-là et chez nous." Song with orchestral accompaniment; words translated from Nekrassov.
Two movements of a Third Symphony in A minor, orchestrated by A. Glazounov.
Finale of Mlada, an unfinished opera-ballet, orchestrated by Rimsky-Korsakov.

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SEPARATION OF COPPER FROM CADMIUM WITH SALICYLALDOXIME IN QUALITATIVE ANALYSIS

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DETECTION of cadmium in solutions containing copper is a common test in qualitative chemical analysis. The usual procedure involves the use of potassium or sodium cyanide as a masking reagent for copper. Some instructors object to the use of cyanide solution on the grounds that it is a hazardous reagent, especially in the hands of beginners.

Various other schemes have been tried as substitutes for the cyanide separation but none of them seems to be entirely reliable for use by inexperienced students. We have tried salicylaldoxime and found it very dependable for the copper-cadmium separation. It is now being used by some of our elementary classes in semimicro qualitative analysis.

Salicylaldoxime is practically a specific reagent for copper in slightly acidic solutions (*4*). The only other substances forming precipitates with the reagent in acid solution are Au^{+++}, OsO_4, Pd^{++}, and VO_3^- (*6*); Fe^{+++} forms a soluble red complex (*4*).

As shown by hydrogen sulfide saturation tests, copper is completely precipitated in acetic acid solutions. The weak yellow-green copper salicylaldoximate is practically insoluble in acetic acid but soluble in mineral acids. The limit of detection for Cu^{++} in slightly acid solution is one part of metal in 2,000,000 of solution (*6*). Cadmium is not precipitated by salicylaldoxime unless the solution is neutral or basic. White cadmium salicylaldoximate is easily soluble in acids or excess ammonia (*6*).

Copper can be quantitatively separated from cadmium with salicylaldoxime by control of acidity (*8*). If one desires to measure the amount of copper by weighing the precipitate as $Cu(C_7H_6O_2N)_2$, the pH value of the acetic acid solution must be 2.6 or greater (*2*). If the reagent is used only to separate out the copper from solution, then the amount of excess acetic acid is not critical.

A one per cent solution of salicylaldoxime is used as the precipitant for copper. One liter of the solution can be prepared, according to Ephraim (*4*), by dissolving 10 grams of salicylaldoxime in 50 ml. ethyl alcohol and pouring the solution into 950 ml. of water at 80°C. This mixture is thoroughly stirred, cooled, and filtered. Another good method for preparation of the solution is given by Astin and Riley (*1*). Dissolve 8.88 grams of salicylaldehyde in 32 ml. of ethyl alcohol and add the solution to 5.08 grams of hydroxylamine hydrochloride dissolved in 8 ml. of water. Dilute the resulting mixture with 80 ml. of ethyl alcohol. Pour the solution into 900 ml. of water at 80°C. Stir well, cool, and filter. Solutions prepared by either of these methods are dependable for use and are fairly stable. They do darken, but solutions several months old still give reliable results.

The separation of copper and the identification of cadmium is simple and reliable. In the usual scheme of qualitative analysis the solution that might contain copper and cadmium has an excess of ammonia, due to the previous separation of bismuth. A deep blue coloration indicates the presence of copper. Add dilute acetic acid dropwise until the blue color turns to green, and then add a few drops more. If the deep blue color is absent but copper is detected by a more sensitive test, add acetic acid until the solution is acid to litmus, and then a few drops more. Add a one per cent solution of salicylaldoxime dropwise until precipitation is complete. Separate the precipitate from the solution and test for complete precipitation. After complete separation of the copper, saturate the clear colorless solution with hydrogen sulfide. A yellow precipitate confirms the presence of cadmium.

Various mixtures of copper and cadmium were satisfactorily analyzed according to these directions. The reagent was used with excellent results in a small summer class in elementary semimicro analysis. The only troubles encountered were due to failure to make the solution acid with acetic acid, which resulted in coprecipitation of the cadmium with the copper, and the darkening of the cadmium sulfide due to incomplete removal of lead or bismuth earlier in the analysis.

From the viewpoint of safety in handling, specificity for copper, and ease in use the reagent is excellent. It is also economical. According to current list prices the cost of one liter of reagent solution prepared from purchased salicylaldoxime is about $1.50, but if the solution is prepared by the method of Astin and Riley, one liter costs only about 18 cents. For semimicro qualitative analysis a liter of solution should suffice for about 1000 separations.

Some instructors will object to the use of salicylaldoxime in qualitative inorganic analysis because the reagent is an organic compound. There is a definite trend toward the use of the more specific oganic reagents for inorganic analysis; salicylaldoxime is one of these. At least 30 published papers deal with its use in analytical chemistry and seven books on inorganic analysis give methods utilizing the reagent (7). Feigl (5) and Engelder, Dunkelberger, and Schiller (3) describe the use of salicylaldoxime for the identification of copper in qualitative analysis. If the objectives of a course in qualitative inorganic analysis include proficiency and accuracy in the analysis of unknown mixtures and acquaintance with reactions that are very useful in analytical chemistry, then salicylaldoxime should be included along with dimethylglyoxime and aluminon as standard reagents for class use.

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Another Periodic Table

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IN THE spring of 1940 the Department of Chemistry at the University of Maine decided to construct a large periodic table for the main lecture room, which would be easily legible at a distance of about 50 feet. While there is nothing new about the way the elements are arranged in this table it does have two novel features which it is the purpose of this paper to describe.

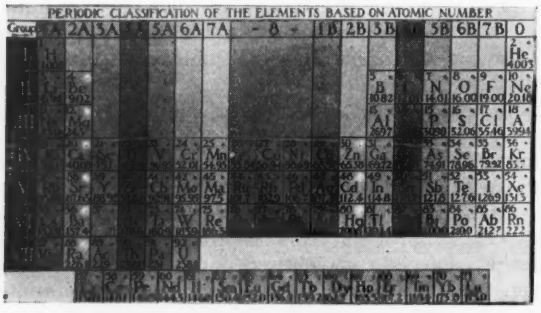

FIGURE 1

Limited space dictated the choice of the arrangement shown in Figure 1, which we consider to be superior to that of Mendeleeff. Its only disadvantage is that it is hard to tell which B group is related to a given A group.

To avoid this difficulty the backgrounds of corresponding A and B groups are painted the same color. This table therefore has all the advantages of the extended arrangement, and also effectively points out the differences between the A and B groups.

The main objection to a colored table such as this is that the tables in textbooks are not colored. We therefore suggest to the students that they color the extended tables in their texts with crayons or water colors.

The second novel feature is a small lamp, controlled by a corresponding switch on the lecture table, in the upper right-hand corner of each square (see Figure 1).

Aside from the spectacular part of this scheme, it enables the lecturer always to face the audience. He does not have to turn around and use a long stick to point out an element. Furthermore, the lights continue to draw attention to the elements as long as the discussion continues.

DETAILS OF CONSTRUCTION

The table shown in Figure 1 is made of a 4 × 8-foot sheet of $^1/_4$-inch plywood. A frame of $^7/_8$-inch pine, the front surface of which is flush with that of the plywood, enlarges it to approximately 5 × 9 feet. The back of the plywood is stiffened by a number of battens, which also serve to hold the chart far enough from the wall to make room for the lamp sockets and wiring.

The squares measure about 6 × 7 inches. It was found by trial that they could not be much smaller. The information that could be included in each square was strictly limited by the fact that *all of it* had to be plainly visible at a distance of 50 feet.

The colors used for the backgrounds are pastel shades that contrast well with each other and with the black lettering. They were modified until a student with rather poor eyesight could read black numbers of the correct size against each color from the back of the lec-

ture room. Flat paint was used throughout. The colors finally adopted are, beginning with Group I: violet, greenish blue, flesh, blue, orange, buff, yellow, and brown. The zero group is white and the rare earths are gray. La and Lu are the same color as Group III. The figures in the space in the sixth period, where elements 57 to 71 belong, are red. The background for the Roman numerals designating the periods is black. The metals are separated from the non-metals by a zigzag red line.

The lamps are flashlight-size pilot lights (type 51, 6–8 v. white bead, 0.2 amp.) with bayonet socket, the latter being used to overcome the effects of possible vibration. The non-metals are designated by lamps colored with shellac containing a red dye. Of course, further relationships can be brought out by using other colors if it seems desirable.

The panel holding the switches is made of "Flexboard" (a material about 1/8 inch thick, containing asbestos). Including an oak frame its dimensions are 15 × 24 inches. As Figure 2 shows, it is essentially a duplicate of the large table, the same background paint being used on both. The lettering on the panel was done with India ink, followed by a coat of label varnish.

The panel is mounted on hinges in an oak box, designed to be set into the lecture table so that its cover will be flush with the table top. Figure 3 shows how the panel is supposed to rise out of the table to form a console.

The S.P.S.T. toggle switches are the usual radio type rated at 250 volts and 3 amperes.

The current is supplied to the lamps by five filament transformers mounted in the oak box. They are connected in parallel and have a combined output of 20

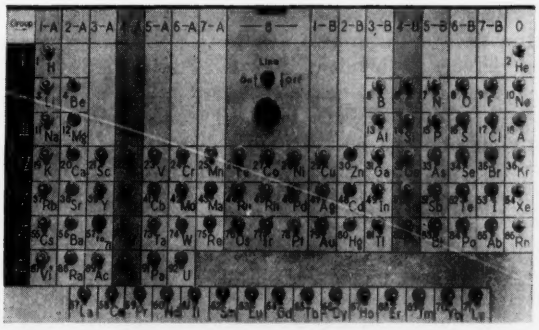

FIGURE 2

amperes at 6.3 volts. Since these transformers cost only seventy-nine cents apiece, five of them were much cheaper than a single transformer with the same output.

The line switch and pilot light, shown in Figures 2 and 3, are in the primary circuit. An automatic switch, that will turn off the primary current when the lid of the control box is closed, can also be installed.

A second-hand telephone cable[1] containing 103 wires (51 pairs and a spare) was used to make connections between the 93 lamps and the corresponding switches. The extra ten wires were used as return leads. If the

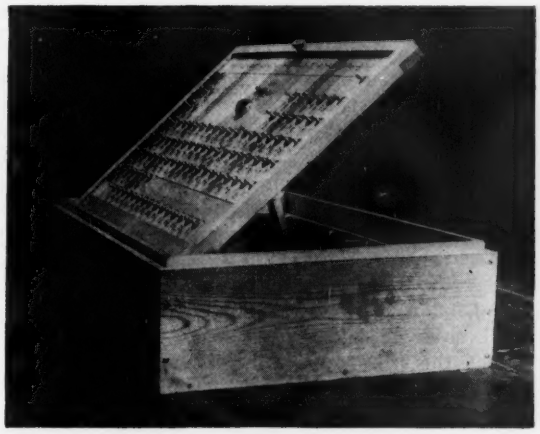

FIGURE 3

cable had contained about 15 more wires, a lamp could have been mounted at the head of each group and the beginning of each period.

The total cost of the whole table was between fifty and sixty dollars.

OPERATION

So far, we have evolved only two tricks for operating the switch board. First, when a whole group or period is to be lighted at one time, it is more dramatic if the primary current is turned off until all the necessary secondary switches are thrown. Second, when a number of squares are lighted, attention can be drawn to one of them by blinking the light.

SUGGESTED VARIATIONS

When this periodic table was being planned, a number of suggestions were made, most of which were rejected because of the cost. Two of them are given here for the benefit of anyone considering a similar project.

The original idea was to build a table with a front made of some translucent material such as tracing cloth. The lamps were to be placed behind the cloth in square boxes so that each light would illuminate a whole square. The colors were to be obtained by using sheets of colored gelatin in front of the lights. Such a scheme would require much larger lamps and wires than those described.

It was also suggested that, by using enough light boxes, both a Mendeleeff and an extended table could be drawn on one long sheet of tracing cloth. By placing rollers at each end of the frame, either table could be brought in front of the lights. A card with the Mendeleeff table on one side and the extended arrangement on the other could be made to fit over the switches in the control box.

[1] Contributed by the New England Telephone and Telegraph Company.

A Study of Interference in Drop Reactions[1]

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THE choice of tests for microchemical qualitative analysis is usually made on the basis of specificity, sensitivity, and availability of the various reagents which react with the substance under consideration. Of these criteria, the most important one is, in most cases, specificity. At present, various investigators are attempting to develop reagents which are specific in their actions, and a book has just been published which treats of "Specific and Special Reactions" (*1*). To date, however, few truly specific reactions have been found, and it is necessary, therefore, to base tests on the use of more general reactions, specificity being obtained through adequate conditioning of the solution to eliminate interferences.

Unfortunately, the interference studies of many tests have been confined to a few common ions or to pertinent analytical groups and so need to be extended. The successful use of general reactions for drop tests depends on the knowledge of possible interferences. In most cases where interferences are known, they may be eliminated by use of simple separations or by application of "inhibiting agents." Because there is such a need for comprehensive interference data in the development of drop reactions, serious consideration should be given this subject. Smith and West (*2*) have made a systematic study of the interferences occurring with tests for 38 different elements. These same authors (*3*) have discussed a method of conducting interference studies and have pointed out the value of classifying the findings as to whether (*a*) the interfering substance gives a false test in the absence of the ion tested for, or (*b*) the interfering substance prevents a true test from forming when the ion tested for is actually present. They proposed that the terms "positive interference" and "negative interference" be applied to types *a* and *b*, respectively. On the basis of this latter report, the following considerations are submitted.

TYPES OF INTERFERENCES

Positive Interference.—This type of interference may be exemplified by the pink inner complex salt formed by dimethylglyoxime and ferrous salts. This color resembles that of the nickel dimethylglyoxime test and so may cause an erroneous reporting of nickel.

Negative Interference.—Negative interferences are those interferences in which a true test is inhibited or retarded. Thus, alkali cyanides react with nickel to give a complex anion which is so slightly dissociated that even the sensitive dimethylglyoxime test may fail to indicate the presence of nickel ions.

Masking Interference.—This type of interference refers specifically to those cases where test colors may be hidden by more intense colors of the interfering ions. Thus, the pink color of a positive dimethylglyoxime test for nickel may be masked if permanganate ions are present. Another example may be cited in the hydrogen peroxide test for vanadium, where the pink color of the positive vanadium test may be masked in the presence of chromium due to the formation of the intensely colored chromate ion.

UTILIZATION OF INTERFERENCE DATA

The most obvious use of interference data is in the interpretation of analytical results. If, for example, a qualitative test by means of dimethylglyoxime indicates the presence of nickel, but subsequent work shows that ferrous iron is present, then the nickel test will be inconclusive since the pink test color would be due, at least in part, to the formation of the ferrous dimethylglyoxime complex. If, however, ferrous iron were absent and a positive test was obtained it would be logical to assume that nickel was present. In case the above test failed to demonstrate the presence of nickel, but subsequent work showed that cyanides were present, the results would be meaningless since the nickel ions would be removed from the zone of reaction in the form of the nickel cyanide complex.

Another valuable use of interference data is in the devising of new tests. Positive interferences serve as an excellent source of new tests. For example, the interference of bivalent iron with the dimethylglyoxime test for nickel may be utilized as a sensitive and useful test for ferrous iron (*4*). Although negative interferences are seldom used as a means of detecting an ion they may serve as useful confirmatory tests. Thus, one of the most reliable tests for mercury is based on the inhibiting action of mercury ions on the starch-iodine reaction (*5*).

A more general use of negative interferences than the one mentioned above is the application of this type of interference to the elimination of interferences in other tests. As has been pointed out before, cyanides interfere negatively with the dimethylglyoxime test for nickel. Also, ferrous iron and nickel both give pink colors or precipitates with this reagent. Knowing all of this, and wishing to test for ferrous iron in the presence of nickel, we can add sufficient alkali cyanide to inhibit the nickel dimethylglyoxime reaction and then test for the iron.

CAUSES OF INTERFERENCES

Positive interferences may be caused by many types of reactions. In most cases, the interfering reactions

[1] Presented before the Division of Analytical and Micro Chemistry at the 101st meeting of the A. C. S., St. Louis, Missouri, April 9, 1941.

are similar in mechanism to the reactions of the true positive test. In the case of the reactions of inorganic substances with organic reagents Feigl (*6*) lists seven types of reactions as being important. These same reactions may be used in explaining certain positive interferences:

Direct synthesis of organic compounds, other than salts.—Ganassini (*7*) noted that bromine can react with fluorescein to form the red tetrabromo-fluorescein. This reaction makes a sensitive test for bromine which is unaffected by chlorine. Iodine, however, gives a positive interference because of the formation of the iodine substitution product which is similar to the bromine derivative.

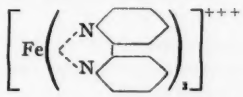
Oxidation or reduction reactions which result in the synthesis of organic compounds.—A very sensitive test for chromate ions is based on the oxidizing action of chromates on acetic acid solutions of benzidine (*8*) with the formation of a blue meriquinoid compound having the following structure:

Vanadates react with benzidine in a similar manner to give the blue oxidation product and therefore interfere positively with this test for chromates.

The inorganic substance may act as a catalyst in the synthesis of organic compounds having distinctive properties.—Because there are so few tests based on the use of catalytic reactions for the synthesis of distinctive organic compounds, it is difficult to find a good example of this type of reaction being the cause of a positive interference. Meigen and Schnerb (*9*) state that tartaric acid is catalytically oxidized to dihydroxymaleic acid by hydrogen peroxide in the presence of ferrous ions. The same reaction takes place if copper salts are substituted for the ferrous iron.

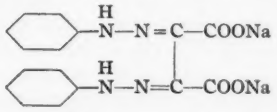
The interfering substance may react to form adsorption compounds possessing distinctive colors.—Magnesium reacts with titan yellow (*10*) to give a distinctive red color. This color is probably due to an adsorption of the dyestuff on magnesium hydroxide. A positive interference is given by aluminum salts, which is very likely caused by an adsorption of the dye on precipitated hydrated aluminum oxide.

Formation of complex ions in which organic molecules are constituents.—α,α'-Dipyridyl reacts with ferrous iron (*11*) to form an intensely colored, water-soluble complex ion of the hexamine type:



Although it is unlikely that such an interference would be encountered in ordinary analytical work, it is possible to have a red precipitate of a cuprous iodide-α,α'-dipyridyl complex which might easily be mistaken for a positive test for ferrous iron.

Formation of normal salts.—Calcium forms insoluble, yellow normal salts with the sodium salt of dihydroxytartaric osazone (*12*), which may be utilized as a test for calcium.



Many other metallic ions, such as zinc, also form normal salts with this reagent and thus give positive interferences.

Formation of inner complex salts.—A good example of this type of interfering reaction is the dimethylglyoxime inner complex salt which this reagent gives with ferrous or nickel ions.

In addition to the typical organic reagent mechanisms mentioned above, positive interferences may be caused by the following types of inorganic reactions:

Double decomposition reactions in which one or more of the products has distinctive properties.—According to Feigl (*13*), calcium may be detected in the presence of strontium and barium by means of the ammonium ferrocyanide reaction. The product in the case is a precipitate of the calcium ammonium ferrocyanide, $Ca(NH_4)_2Fe(CN)_6$. A positive interference with this reaction is given by magnesium which reacts in an analogous manner to give a reaction product of magnesium ammonium ferrocyanide.

Catalytic or induced reactions.—Copper may be detected by means of the thiosulfate-ferric iron reaction which is catalytically accelerated in the presence of copper salts (*14*).

$$2Fe^{+++} + 2S_2O_3^{--} \longrightarrow 2Fe^{++} + S_4O_6^{-4}$$

By using alkali thiocyanate ions to indicate the concentration of ferric ions, it is possible to detect small quantities of copper, since the red color of the ferric thiocyanate complex will be faded more quickly in a copper-containing test drop than in a copper-free blank. A positive interference with this reaction occurs in the presence of arsenic salts which have the same catalytic effect as copper.

Formation of complex ions possessing distinctive properties.—Molybdenum may be detected by its reaction with potassium thiocyanate (*15*). This test is carried out by first reducing the molybdenum to the pentavalent state, by means of stannous chloride or zinc, after which it reacts with thiocyanates to give a red color. Ferric iron may give a positive interference, when present in excessive amounts, due to the formation of the familiar red complex $[Fe(CNS)_6]^{---}$. This interference can be avoided by adding sufficient reducing agent to convert all of the iron to the ferrous condition, which does not interfere.

Oxidation-reduction reactions which produce compounds having distinctive properties.—Titanium is commonly detected by means of the yellow color which results from the reaction between hydrogen peroxide and acid solutions of titanium salts (*16*). Chromium

gives a positive interference with this test since it is oxidized to the yellow chromate ion, CrO_4^{--}.

The discussion of the causes of interferences has, thus far, been confined to the considerations of "false tests," or positive interferences. Of equal importance, both from the standpoint of practical application and from the standpoint of its theoretical significance, is the subject of negative interferences or inhibiting reactions. The causes of negative interferences are many, although the largest proportion are probably due to the formation of complex ions. The interfering reaction mechanism may involve the rate of speed of the test reaction, or it may affect the concentration of the test reaction products by causing a shift in the chemical equilibrium. The following are the principal types of reactions which can cause negative interferences:

Poisoning of catalysts.—One of the most delicate tests for the platinum metals is the so-called "glow" reaction (*17*). This catalytic test is based on the fact that platinum metals are able to condense gases, such as hydrogen, on their surfaces. Hydrogen, so condensed, reacts with the oxygen of the air and liberates heat which is adsorbed by the metal to give a bright spot of red-hot metal. Arsenic, in large amounts, retards this catalytic action of the platinum metals and thus interferes negatively with the test.

Negative catalysts.—To date little attention has been paid to possible negative catalysts in analytical chemistry. Careful study would probably show that a number of negative interferences are due to the effect of negative catalysts, especially in the case of oxidation-reduction reactions. Klemenc and Pollak (*18*) have shown, for example, that the oxidation of arsenious acid by nitric acid may be slowed up by the negative catalytic effect of mercuric mercury.

Mass action effects.—Many spot tests for magnesium are based on the precipitation of magnesium hydroxide with subsequent adsorption of a suitable dyestuff on the precipitate. Such a series of reactions is utilized in the quinalizarin test for magnesium as described by Hahn (*19*). This test decreases in sensitivity when large amounts of ammonium salts are present. This interference may be attributed to the reduction in hydroxyl ion concentration which results from the mass action effect of the ammonium ions on the dissociation of the ammonium hydroxide, or ammonia water. Lowering the concentration of the hydroxyl ions reduces the amount of magnesium hydroxide formed, and consequently reduces the sensitivity of the test.

Competitive reactions, other than complex ion formation, which reduce the concentration of either the ion tested for or the reagent.—Uranyl salts may be detected by adding a drop of the slightly acid test solution to filter paper which has previously been impregnated with potassium ferrocyanide (*20*). In the presence of uranium a brownish red stain is formed. Zinc salts give a negative interference with this test since they react preferentially with the reagent to form white zinc ferrocyanide, $Zn_3Fe(CN)_6$, and so tend to prevent the uranyl-ferrocyanide reaction from taking place.

Reduction in the effective concentration of either the ion to be tested for or the reagent, through formation of complex ions.—Certain tests for platinum, as for example, the potassium iodide test (*21*), may be completely inhibited in the presence of excess thiocyanate ions. The interference in this case is probably due to the formation of complex platinithiocyanate ions, $[Pt(CNS)_6]^{--}$, which are so slightly dissociated that there are insufficient platinum ions in solution to give the test. Other more commonly known complexes which tend to produce negative interferences with their respective ions include the following: ferric complexes of the general type $[FeX_6]^{---}$, where X may be F^-, CNS^-, $HAsO_4^{--}/2$, $PO_4^{---}/3$, citrate/3, tartrate/2, $C_2O_4^{--}/2$, CN^-, etc.; aluminum complexes, $[AlX_6]^{---}$, where X may be F^-, $C_2O_4^{--}/2$, or tartrate/2; mercuric complexes, $[HgX_4]^{--}$, where X may be CN^-, CNS^-, or I^-.

METHOD OF STUDYING INTERFERENCES

In the discussion of the theoretical aspects of interferences it has been pointed out that interference data should be classified as to type. Also, it was shown that interference data can serve three fundamental purposes: first, they are invaluable in the interpretation of analytical results; second, they may serve as a source of new tests; and third, they serve as a source of knowledge concerning possible "inhibiting agents" which may be used in preventing interferences with other tests. Because of the varied uses to which such data are put, interference studies should be as comprehensive as possible. Thus, in the case of a practical analytical problem, it is unlikely that oxalates would be present to interfere with a test for platinum. Consequently, from the standpoint of interpretation of analytical results, it is relatively unimportant to know that oxalates can completely inhibit the benzidine test for platinum. However, it is of value that platinum can be "tied up" in the form of a platinum-oxalate complex and so be prevented from interfering with the benzidine test for gold.

Having in mind the various purposes for which the data may be used, it is proposed that interference studies include the ions listed in Table 1. The standard solutions listed are made up to contain 10 mg. per ml. of each ion. In the case of the compounds listed under "miscellaneous substances", there are included those substances which do not fit in readily under the regular groups of the periodic table. In general, they include substances which might be likely to give negative interferences and thus be of potential value as "inhibiting agents" for preventing interferences with other tests.

The actual laboratory study of interferences should be carried out according to some systematic scheme, as for example the following:

Blank
Control

(*a*) 10 mg. per ml.
(*b*) 1 mg. per ml.

TABLE 1

STANDARD SOLUTIONS FOR INTERFERENCE STUDIES

Ion	Weight of Salt per 50 ml. Solution	Ion	Weight of Salt per 50 ml. Solution
Group I			
Li^+	4.94 g. $LiNO_3$	Rb^+	0.863 g. $RbNO_3$
Na^+	1.85 g. $NaNO_3$	Ag^+	0.787 g. $AgNO_3$
K^+	1.29 g. KNO_3	Cs^+	0.733 g. $CsNO_3$
Cu^{++}	2.33 g. $Cu(NO_3)_2 \cdot 6H_2O$	Au^{+++}	0.770 g. $AuCl_3$
Group II			
Be^{++}	10.4 g. $Be(NO_3)_2 \cdot 3H_2O$†	Cd^{++}	1.37 g. $Cd(NO_3)_2 \cdot 4H_2O$
Mg^{++}	5.17 g. $Mg(NO_3)_2 \cdot 6H_2O$	Ba^{++}	0.951 g. $Ba(NO_3)_2$
Ca^{++}	2.95 g. $Ca(NO_3)_2 \cdot 4H_2O$	Hg^{+}	0.700 g. $HgNO_3 \cdot H_2O$†
Zn^{++}	2.28 g. $Zn(NO_3)_2 \cdot 6H_2O$†	Hg^{++}	0.831 g. $Hg(NO_3)_2 \cdot {}^1/_2H_2O$‡
Sr^{++}	1.62 g. $Sr(NO_3)_2 \cdot 4H_2O$		
Group III			
BO_2^-	0.769 g. $NaBO_2$	Y^{+++}	1.85 g. $Y(NO_3)_3 \cdot 3H_2O$
$B_4O_7^{--}$	0.569 g. $Na_2B_4O_7 \cdot 10H_2O$	In^{+++}	1.66 g. $In(NO_3)_3 \cdot 4^1/_2H_2O$
Al^{+++}	6.95 g. $Al(NO_3)_3 \cdot 9H_2O$	La^{+++}	2.59 g. $La(NO_3)_3 \cdot 6H_2O$
Sc^{+++}	2.56 g. $Sc(NO_3)_3$	Ce^{+++}	1.55 g. $Ce(NO_3)_3 \cdot 6H_2O$
Ga^{+++}	1.83 g. $Ga(NO_3)_3$	Tl^{+}	0.652 g. $TlNO_3$
Group IV			
CO_3^{--}	0.883 g. Na_2CO_3	Sn^{++}	0.957 g. $SnCl_2 \cdot 2H_2O$*,§
SiO_3^{--}	0.597 g. $Na_2SiO_3 \cdot 9H_2O$	Sn^{++++}	1.10 g. $SnCl_4$§
Ti^{++++}	1.98 g. $TiCl_4$§	Pb^{++}	0.799 g. $Pb(NO_3)_2$
GeO_3^{--}	0.796 g. GeO_2‖	Zr^{++++}	2.35 g. $Zr(NO_3)_4 \cdot 5H_2O$†
		Th^{++++}	1.50 g. $Th(NO_3)_4 \cdot 12H_2O$†
Group V			
NH_4^+	2.22 g. NH_4NO_3	HPO_4^{--}	1.86 g. $Na_2HPO_4 \cdot 12H_2O$
NO_2^-	0.862 g. $NaNO_2$*	$P_2O_7^{-4}$	0.764 g. $Na_4P_2O_7$*
NO_3^-	0.749 g. $NaNO_3$	V^{+++}	1.54 g. VCl_3
$H_2PO_2^-$	0.508 g. NaH_2PO_2	VO_3^-	0.586 g. $NaVO_3 \cdot 16H_2O$
HPO_3^{--}	0.636 g. $Na_2HPO_3 \cdot 5H_2O$*	$HAsO_3^{--}$	0.686 g. Na_2HAsO_3
$P_4O_{13}^{-6}$	0.708 g. $Na_6P_4O_{13}$*	$HAsO_4^{--}$	0.565 g. $Na_2HAsO_4 \cdot 12H_2O$
$P_6O_{18}^{-6}$	0.646 g. $(NaPO_3)_6$*	Sb^{+++}	0.936 g. $SbCl_3$§
PO_3^-	0.611 g. $NaPO_3$*	Sb^{+++++}	1.23 g. $SbCl_5$§
		Bi^{+++}	1.16 g. $Bi(NO_3)_3 \cdot 5H_2O$†
Group VI			
S^{--}	1.22 g. Na_2S	SeO_4^{--}	0.661 g. Na_2SeO_4
$S_2O_3^{--}$	0.614 g. $Na_2S_2O_3 \cdot 5H_2O$*	MoO_4^{--}	0.617 g. $Na_2MoO_4 \cdot 2H_2O$
SO_3^{--}	0.787 g. Na_2SO_3	TeO_3^{--}	0.629 g. Na_2TeO_3
SO_4^{--}	0.740 g. Na_2SO_4	TeO_4^{--}	0.620 g. Na_2TeO_4
Cr^{+++}	3.85 g. $Cr(NO_3)_3 \cdot 9H_2O$	WO_4^{--}	0.581 g. $Na_2WO_4 \cdot 2H_2O$
$Cr_2O_7^{--}$	0.591 g. $Na_2Cr_2O_7$	UO_2^{++}	0.927 g. $UO_2(NO_3)_2 \cdot 6H_2O$
CrO_4^{--}	0.698 g. Na_2CrO_4	UO_4^{--}	0.535 g. Na_2UO_4¶
SeO_3^{--}	0.683 g. Na_2SeO_3		
Group VII			
F^-	1.11 g. Na_2F_2	Br^-	0.644 g. NaBr
Cl^-	0.824 g. NaCl	BrO_4^-	0.590 g. $NaBrO_3$
ClO_3^-	0.638 g. $NaClO_3$	I^-	0.591 g. NaI
ClO_4^-	0.616 g. $NaClO_4$	IO_3^-	0.566 g. $NaIO_3$
Mn^{++}	2.61 g. $Mn(NO_3)_2 \cdot 6H_2O$	ReO_4^-	0.546 g. $NaReO_4$
MnO_4^-	0.567 g. $NaMnO_4 \cdot 3H_2O$		
Group VIII			
Fe^{++}	2.58 g. $Fe(NO_3)_2 \cdot 6H_2O$*	Rh^{+++}	2.58 g. $Rh(NO_3)_3 \cdot 2H_2O$
Fe^{+++}	3.13 g. $Fe(NO_3)_3 \cdot 6H_2O$	Pd^{++}	0.832 g. $PdCl_2$
Co^{++}	2.47 g. $Co(NO_3)_2 \cdot 6H_2O$	Os^{+++}	3.03 g. $\frac{1}{2}(OsCl_3 \cdot 3KCl) \cdot 6H_2O$
Co^{+++}	1.40 g. $CoCl_3$	Ir^{++++}	0.867 g. $IrCl_4$
Ni^{++}	2.48 g. $Ni(NO_3)_2 \cdot 6H_2O$	Pt^{++++}	0.864 g. $PtCl_4$
Ru^{+++}	2.94 g. $Ru(NO_3)_3 \cdot 6H_2O$		
Miscellaneous Substances			
CN^-	0.533 g. NaCN	Lactate	1% soln. of the acid
$Fe(CN)_6^{---}$	0.650 g. $Na_3Fe(CN)_6 \cdot H_2O$*	Gluconate	1% soln. of the acid
$Fe(CN)_6^{----}$	1.05 g. $Na_4Fe(CN)_6 \cdot 10H_2O$	Glycol	1% solution
CNS^-	0.699 g. NaCNS	Diethylene glycol	1% solution
Acetate	1% soln. of the acid	*i*-Inositol	1% solution
Oxalate	1% soln. of the acid	Sorbitol	1% solution
Malonate	1% soln. of the acid	Mannitol	1% solution
Adipate	1% soln. of the acid	Sucrose	1% solution
Succinate	1% soln. of the acid	Dextrose	1% solution
Phthalate	1% soln. of the acid	Aniline	1% solution
Tartrate	1% soln. of the acid	Pyridine	1% solution
Citrate	1% soln. of the acid		

* Make up fresh.
† Make slightly acidic with HNO_3.
‡ Dissolve in HNO_3 and dilute. Add a globule of mercury to prevent oxidation.
§ Keep in solution by means of HCl.
‖ Dissolve in NaOH and dilute with water.
¶ Dissolve in 3 ml. acetic acid and dilute.

Check for positive interferences (reagent plus ions of Groups I, II, etc.)

Check for negative and masking interferences (ions of Groups I, II, etc., plus ion being tested for, plus reagent)

The results of such studies should be classified and, whenever possible, expressed semiquantitatively.

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DIVISION OF CHEMICAL EDUCATION OF THE AMERICAN CHEMICAL SOCIETY

MINUTES OF EXECUTIVE COMMITTEE MEETING

Atlantic City, September 9, 1941

PRESENT: R. D. Reed, Chairman, N. D. Cheronis, N. W. Rakestraw, Virginia Bartow, and P. H. Fall.

The treasurer gave her report, which was accepted, as follows:

Cash in bank—April 2, 1941	$97.04
Receipts from dues	15.00
Receipts from M. V. McGill from "Supplementary Experiments"	50.00
	$162.04
Expenditures:	
Ind. Eng. Chem. Abstracts—St. Louis Meeting	$22.20
B. C. Hendricks Committee on Examinations and Tests	50.00
V. Bartow—Office of Treasurer	10.14
P. H. Fall—Office of Secretary	15.00
	$97.34
Receipts less expenditures	$64.70
Cash in bank—September 2, 1941	$64.70

No withdrawals from savings account

VIRGINIA BARTOW, *Treasurer*

Motion carried that bills for printing letterheads and envelopes for Office of Secretary ($16.67 by Mack Printing Company) and reprints of Abstracts (Separates) for Atlantic City Meeting ($10.43—*Ind. Eng. Chem.*) be paid.

Suggestion was made that the B. S. Hopkins Committee on High-School Chemistry be asked to present before one of our Divisional meetings a report of its findings.

T. A. Ashford of Chicago, and Laurence S. Foster of Brown University were elected to the Committee on Examinations and Tests to succeed R. E. Kirk and F. B. Wade, whose terms expire.

T. D. Kelsey of Grover Cleveland High School, St. Louis, and T. A. Ashford of Chicago were elected to the Committee on High-School Chemistry to succeed two former members, Dr. Davis, deceased, and N. D. Cheronis, retiring from the Committee.

MINUTES OF BUSINESS MEETING OF THE DIVISION

Atlantic City, September 10, 1941

Dr. W. H. Fulweiler, a consulting chemist, spoke of the great need of obtaining sufficient steel, magnesium, aluminum, rubber, and other materials by manufacturers of scientific materials and instruments if we are to avoid a disastrous shortage of testing materials and necessary laboratory equipment for industrial and instructional laboratories. Our Division was asked to aid in bringing to the attention of the proper government officials the urgent necessity of allowing manufacturers of scientific materials to secure the very essential, though relatively small amounts of raw materials needed.

Motion was made and carried that the Chairman of our Division appoint a Committee to take action as suggested by Dr. Fulweiler. The Chairman thereupon appointed S. R. Brinkley of Yale as Chairman of such a Committee, with power to act and to choose any additional members he may desire.

The Treasurer's report, given in detail above, was presented and accepted. The Secretary reported on the meeting of the Executive Committee on the previous day (see above).

N. D. Cheronis spoke of the importance of technical and non-collegiate chemistry and moved that a Committee be appointed by the Chairman to study this problem. The motion was carried.

O. M. Smith, Chairman of the Committee on Examinations and Tests, gave a progress report on the work of his committee. Fifteen men spent a week in conference at the University of Chicago this summer to reformulate the objectives of the General Chemistry Examination and to construct test items for the 1942 form. He stated that his committee feels that there is definite need for a committee to make a study of our methods of teaching in colleges and universities. There is need for statistical material on our type of teaching; *e. g.*, the value of laboratory work versus none, or versus lecture demonstrations.

Motion made and carried that a Committee be appointed to study the Problems of Teachers of Chemistry in Colleges and Universities.

The Nominating Committee consisting of O. M. Smith, Chairman, Ed. F. Degering, and Ross A. Baker presented the following as nominees for officers for the year September, 1941–September, 1942:

F. E. Brown, Chairman, Iowa State College, Ames, Iowa
A. J. Currier, Vice Chairman, Pennsylvania State College, State College, Pennsylvania
C. E. White, Treasurer, University of Maryland, College Park and Baltimore, Maryland
Laurence L. Quill, Member-at-Large, Ohio State University, Columbus, Ohio

There being no nominations from the floor, motion was made and carried that the Secretary cast a unanimous ballot for the nominees, just named.

Motion carried that the Division send a resolution of appreciation to retiring treasurer, Dr. Virginia Bartow, of the University of Illinois, who has served the Division as treasurer for ten years.

PAUL H. FALL, *Secretary*

Rare Gases in Everyday Use

F. P. GROSS, JR.

Air Reduction, New York City

CAVENDISH in 1785 was the first to suspect that the atmosphere contained gases other than phlogisticated air (nitrogen) and dephlogisticated air (oxygen). He found that a discharge of electricity in air caused the nitrogen and oxygen to combine and the product resulting could be absorbed chemically. The volume thus continually diminished and, by persistent sparking of the mixture with additional oxygen, the nitrogen was finally removed. A small volume of gas remained which resisted all efforts to remove it.

Cavendish had actually isolated a mixture of rare gases but the spectroscope, by which the gas might have been recognized to be new, was not invented and the quantity was so small that he did not pursue the subject. His published statement, "If there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $^1/_{120}$ part of the whole," was a remarkably close estimate of the quantities of rare gases present in the atmosphere. One hundred years or more lapsed before Cavendish's observation was clarified and it remained for others to separate and identify the five rare gases.

In 1868, Lockyer detected a yellow line in the spectrum of the sun which was not reproduced in the spectrum of any of the substances then known on earth. The line was conspicuous and was attributed by him to the presence of a chemical element existing in the sun. The name given to the new element was "helium," from the Greek word meaning "the sun."

In 1894, Lord Rayleigh observed that the density of nitrogen gas derived from air was consistently higher than that of nitrogen made by chemical means. Sir William Ramsay collaborated with Rayleigh and their joint efforts led to the discovery of a gas which constitutes 1.3 per cent by weight or 0.94 per cent by volume of the atmosphere. The presence of rare gases in "nitrogen" from the atmosphere caused it to weigh more than nitrogen produced chemically, which did not contain them.

To the astonishment of the discoverers, the new gas was found not to enter into any sort of chemical combination and it was named "argon" on this account, from the Greek word meaning "inactive."

Soon after the discovery of argon, Ramsay, in search for other sources, examined the gas obtained by heating a mineral called clevite, which W. F. Hillebrand of the United States Geological Survey had reported previously. It was first suspected that this gas was argon but on examination its spectrum showed that, while argon was present, the gas was principally helium. In the same year, 1895, Kayser reported the presence of helium in the atmosphere, having detected its presence spectroscopically.

Ramsay, from a study of the periodic table, reasoned that another inert gas should exist between helium and argon. He searched for possible sources of this new element without success but finally obtained a clue from the fact that by diffusion "argon" could be separated into a lighter and heavier portion.

A simple method for separating a mixture of gases is to liquefy the mixture and, as it boils, collect fractions of the vapors. This was the principle which Ramsay and Travers used in their search for the suspected element, which was finally successful in 1898. Ramsay allowed 15 liters of liquid argon to vaporize and the first fraction to boil off was found to be lighter than argon. It was studied with the aid of the spectroscope and found to be, as suspected, a new gas. It was named "neon" from the Greek word meaning "new one."

Heavier gases were found in the residue obtained from the slow evaporation of liquid air. The first of these was called "krypton," or "hidden one," and the last was named "xenon," or the "stranger."

The final major development in the history of these gases occurred in 1907 when Cady and McFarland reported the presence of helium in a number of natural gases, mainly from Kansas, in some cases as much as two per cent by volume. This potential source of supply occasioned the action of the Federal Government at the time of the World War in 1917 to develop and build plants for obtaining helium in quantity.

PROPERTIES OF THE RARE GASES

The rare gases are all colorless, odorless, and tasteless; they are non-inflammable and non-explosive. There appears to be a general gradation of certain physical properties in this family beginning with helium and running through neon, argon, krypton, and xenon. This is to be noted, for instance, with respect to density, molecular weight, refractive index, dispersion, and boiling and melting points. In some properties, such as heat conduction, solubility in water, and compressibility, for example, the progression is broken to some extent. All are monatomic.

These gases are characterized by their extreme chemical inactivity. While one or two compounds of certain rare gases are reported to have been prepared, such researches and the results obtained may be considered of scientific interest only. For all practical purposes these gases are to be considered non-reactive. The "rare," or "noble" gases, named by reason of their comparative scarcity, are therefore also known as "inert"

gases. Their aloofness characterizes them as the aristocrats of the family of chemical elements.

RECOVERY OF RARE GASES FROM THE ATMOSPHERE

With the exception of helium, the source of the rare gases commercially today is the atmosphere. The following table gives the quantities of the gases contained in air; those for the major constituents are quite accurate, but the figures for the minor constituents should be considered close approximations only.

	Composition of the Atmosphere	
	By Volume	*By Weight*
Nitrogen	78.03%	.....
Oxygen	20.99%	.....
Argon	0.94%	.....
Carbon dioxide	0.031%	.....
Neon	1 part in 65,000	1 pound in 44 tons
Helium	1 part in 200,000	1 pound in 725 tons
Krypton	1 part in 1,000,000	1 pound in 173 tons
Xenon	1 part in 11,000,000	1 pound in 1208 tons

Today we are accustomed to regard argon, neon, helium, and even krypton and xenon as commonplace, but their classification as "rare gases" is justified. The quantities above are small. For example, it has been suggested that to inhale the same volume of xenon from the air as one breath of air, an individual would have to breathe steadily for a period considerably longer than a year.

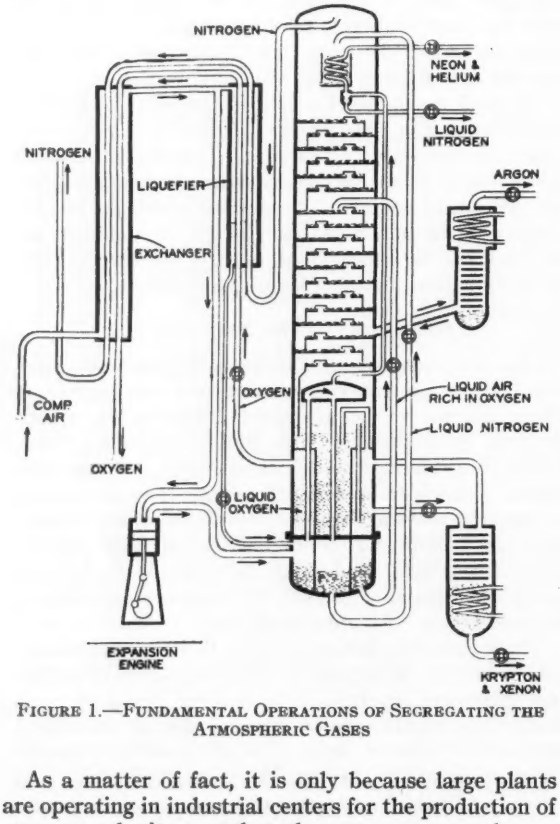

FIGURE 1.—FUNDAMENTAL OPERATIONS OF SEGREGATING THE ATMOSPHERIC GASES

As a matter of fact, it is only because large plants are operating in industrial centers for the production of oxygen and nitrogen that the rare gases can be recovered today at a cost which permits commercial utilization. Air liquefaction plants provide crude gas mixtures which contain the rare gases in higher concentrations than they occur in air and from which they can be economically separated and purified.

The underlying principle involved in the production of atmospheric gases by liquefaction methods is shown in Figure 1, including the manner in which each of the rare gases may be segregated and removed from the system. Pressures, details of construction, course of flow through the system as a whole, etc., will differ considerably in the several processes now operating for the production of these gases, but the fundamentals are similar in all of them.

Air, as the source of raw material, is cleaned and compressed and then cooled by passing it counter-current to outgoing gases from the liquefaction column. In the Claude process the incoming air at this point is separated into two portions, one of which passes to a liquefier for further heat interchange with the cold gases coming from the column; the other is made to do work in an expansion engine. This operation has a further refrigerating effect, liquefying the air.

Air in the liquid state is passed through a series of fractional distillations in a rectification column. It is possible to separate one constituent from another because of the fact that the constituents boil at different temperatures and the vapor from a liquid of given composition is richer than the liquid in the lower boiling constituent. The rectification column merely repeats this process many times until substantially pure nitrogen is produced at one end of the column and substantially pure oxygen at the other.

From the boiling points of the gases (Table 1) we can determine what separation takes place during the fractional distillation process. Nitrogen, neon, and helium, having lower boiling points, will distil over first, leaving oxygen, argon, krypton, and xenon in the residual liquid. A second fractionation of this argon-oxygen mixture provides the partial separation to give us oxygen 99.5 per cent pure and a raw argon approximately 50 per cent pure. The raw argon is further purified chemically by removal of the major portion of oxygen by burning it with hydrogen and then by passing the gas over hot copper and copper oxide to remove the last traces of oxygen, as well as any excess hydrogen remaining.

Krypton and xenon are collected in the residual liquid from the liquefaction column and are purified and separated by physical means in the laboratory.

Nitrogen, like oxygen, may be produced 99.5 per cent pure at the column, but the neon-helium mixture must be treated further to remove the nitrogen impurity; then the two rare gases are separated from each other.

Purification and separation of the crude neon-helium and krypton-xenon mixtures involve operations wherein nitrogen, oxygen, and water vapor are removed chemically. The rare gases are finally purified by selective adsorption in charcoal at low temperature.

TABLE - I

PHYSICAL CONSTANTS OF THE ATMOSPHERIC GASES

SUBSTANCE	FORMULA	MOLECULAR WEIGHT 1939	D_{70}	V_{70}	D	P_c	T_e	T_f	T_c	C_p	C_v	H_e	H_f	H_s	$K_{\times 10^5}$	I_p	FORMULA
NITROGEN	N_2	28.016	0.07247	13.80	1.25049	33.490	-195.808	-210.02	-147.16	0.2481 @ 20°C.	0.1774 @ 20°C.	47.58	7.81	—	58.0 @ 0°C.	16.9	N_2
OXYGEN	O_2	32.0000	0.08281	12.08	1.42895	49.713	-182.970	-218.4	-118.84	0.2187 @ 20°C.	0.1566 @ 20°C.	50.9	3.32	—	58.3 @ 0°C.	—	O_2
HELIUM	H_e	4.003	0.01034	96.71	0.17846	2.26	-268.92	-272.1	-267.95	1.251 @ 18°C.	0.752	5.7	0.835 @ -270.4°C	—	34.3 @ 0°C.	25.6	H_e
ARGON	A	39.944	0.1034	9.671	1.78394	47.996	-185.86	-189.26	-122.46	0.1252 @ 17.8°C.	0.075 @ 15°C.	38.9	7.01	—	38.2 @ 0°C.	15.1	A
NEON	N_e	20.183	0.05215	19.17	0.89990	26.86	-246.087	-248.61	-228.75	———	Y=1.642	20.8	3.97 AT THE TRIPLE POINT	—	111.2 @ 0°C.	21.5	N_e
XENON	X_e	131.3	0.3417	2.926	5.896	58.20	-108.06	-112.0	16.6	———	Y=1.666 @ 19°C.	23.0	4.18 AT THE TRIPLE POINT	—	12.4 @ 0°C.	11.5	X_e
KRYPTON	K_r	83.7	0.2169	4.610	3.743±0.001	54.182	-153.23	-157.0	-63.77	———	Y=1.689	25.78 ±.03	4.67 AT THE TRIPLE POINT	—	21.2 @ 0°C.	13.3	K_r
CARBON DIOXIDE	CO_2	44.010	0.1146	8.7291	1.97682	72.92	T_s=-78.43	———	31.34	0.1998 @ 20°C.	0.1543 @ 18°C.	83.25 AT THE TRIPLE POINT	55 AT THE TRIPLE POINT	137.0	34.7 @ 0°C.	14.3	CO_2

LEGEND

D_{70} = DENSITY IN LBS. PER CU. FT. AT 70°F. AND 1 ATMOSPHERE.	C_p = SPECIFIC HEAT AT CONSTANT PRESSURE IN CALORIES PER GRAM.
V_{70} = VOLUME IN CU. FT. PER LB. AT 70°F. AND 1 ATMOSPHERE.	C_v = SPECIFIC HEAT AT CONSTANT VOLUME IN CALORIES PER GRAM.
D = DENSITY IN GRAMS PER LITER AT N.T.P.	H_e = LATENT HEAT OF EVAPORATION AT NORMAL BOILING POINT, OR AT STATED PRESSURE, IN CALORIES PER GRAM.
P_c = CRITICAL PRESSURE IN ATMOSPHERES.	H_f = LATENT HEAT OF FUSION AT NORMAL FUSION POINT IN CALORIES PER GRAM.
T_e = TEMPERATURE IN °C. OF SATURATED VAPOR AT 1 ATMOSPHERE.	H_s = LATENT HEAT OF SUBLIMATION AT NORMAL SUBLIMATION POINT, OR AT STATED PRESSURE, IN CALORIES PER GRAM.
T_f = NORMAL FREEZING OR MELTING TEMPERATURE IN °C. AT 1 ATMOSPHERE.	K = THERMAL CONDUCTIVITY.
T_c = CRITICAL TEMPERATURE IN °C.	I_p = IONIZATION POTENTIAL IN VOLTS.
T_s = NORMAL SUBLIMATION TEMPERATURE IN °C. AT 1 ATMOSPHERE.	Y = $C_p \div C_v$

COMMERCIAL APPLICATIONS OF RARE GASES

The commercial application or utilization of the rare gases was retarded originally because they are inert. However, the present applications depend principally upon this characteristic and it is because they do not react chemically that they perform their work so well.

Argon

The first major application is found in the use of argon in the incandescent lamp industry, which today consumes tens of thousands of cubic feet per month. The emission of light from a heated tungsten wire increases as the temperature of the wire is raised. In a vacuum a tungsten filament will vaporize more readily at the same temperature than in a gaseous atmosphere under pressure. Therefore, if tungsten is maintained under pressure of one atmosphere at a temperature just below its volatilization point, more light is emitted than is possible with the same wire in a vacuum. Since tungsten combines readily with most gases, this pressure is advantageously maintained by the use of an inert gas, preferably of high density.

The first gas-filled lamps contained nitrogen but argon is more suitable for this use because its thermal conductivity is lower and because, unlike nitrogen, it is inert under all conditions regardless of temperature. The lower thermal conductivity of argon means better insulation against loss of heat from the filament and consequently a higher filament temperature from the same current. It is possible to operate a lamp in an argon atmosphere for longer periods of time at a higher temperature than in a nitrogen atmosphere. For these reasons, the efficiency of an argon-filled lamp is greater.

In a manner similar to its use in incandescent lamps, argon is used in certain of the newer types of bulbs or tubes for production of ultra-violet radiation. Its action here again is passive, for the ultra-violet light is produced from the mercury arc, and the argon itself simply serves as an ionizing medium with satisfactory electrical characteristics for starting operation of the lamp.

There are other uses for argon, such as in the manufacture of rectifying tubes for delivering direct current from a source of alternating current. It is also used pure, or admixed with other rare gases, in the manufacture of many of the well-known luminous tubes.

Neon

Neon is characterized by its high electrical conductivity and light-emissive powers when an electrical current is discharged through it and is, in fact, most unusual. It is exceedingly sensitive to such discharges of electricity; at pressures in the neighborhood of 5 mm. it possesses remarkable properties, being ionized by charges of electrical energy of high potential but low energy content. Shaking a tube containing a bit of mercury sealed in with pure neon will cause the neon to glow.

Neon has given its name to the tubular lights, gaseous conductor lamps, used in advertising and, more recently, for illumination. Since these lamps are popularly known as "neon tubes," it is fitting and histori-

cally justified that the subject be reviewed under "neon" even though other rare gases or mixtures are frequently used.

Historically, the first luminous tubes, or gaseous conductor lamps, did not call for the use of rare gases. The so-called Moore tubes were used from 1904 to 1910 for illumination and these tubes were filled with nitrogen or carbon dioxide.

In 1910 a Frenchman, Georges Claude, who earlier perfected one of the liquefaction processes now used for the separation of the atmospheric gases, introduced the neon tube for display advertising. This rare gas tube overcame the major difficulties of the Moore lamp because of its higher electrical conductivity and because of the greater stability of the gaseous filling, which resulted in relatively long life of the tube. During the World War little of importance developed, but in the early '20's luminous display tubes began to appear in outdoor advertising in this country, and by 1925 a number of concerns were engaged in their production. By 1930 it was estimated that 50 per cent of the bulb signs in the United States had been replaced by neon tubes.

Gaseous conductor lamps are essentially glass containers filled with a gas at low pressure and equipped with electrodes for producing an electrical discharge through the gas. Passage of an electric current between the electrodes causes the gas to become luminous.

Classification of Gaseous Conductor Lamps

1. Negative glow lamps, which are characterized by two electrodes spaced relatively near each other. Light is emitted by the gas immediately surrounding the negative electrode (cathode), where the electrons pass from the metal to the gas.

2. Positive column lamps, which have electrodes spaced relatively far apart as in the display sign tube. Light is emitted by the column of gas extending from a point near the positive electrode (anode) to a point near the negative electrode.

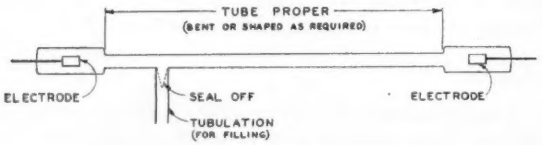

FIGURE 2

Each of these classes may be further divided into hot cathode and cold cathode lamps. In the former, the cathode is heated to a high temperature by the current whereas in the latter the cathode operates at a relatively low temperature. Since a hot electrode emits electrons more readily than a cold electrode, hot cathode lamps operate at lower voltages than the cold cathode type.

The ability of a gas or vapor to become luminescent, under the influence of the flow of electrons through it, involves a theory of the structure of atoms. As encounters take place between electrons and the atoms or molecules of the gases or vapors present, there results a state of excitation. Light is produced, which comes about from the energy given up as the disturbed molecule, atom, or ion settles down to its stable or neutral state. The color of the light or the nature of its radiation will depend on the nature of the gas or vapor, its atomic structure, its density, and upon other factors. This series of encounters between electrons, atoms, and ions has been likened to a bowling ball striking a set of tenpins.

The commercial sign tube (Figure 2) is essentially a section of glass tubing bent to shape as desired, with an electrode sealed into each end, and filled with a rare gas. The gases commonly used in modern advertising tubes are neon, argon, helium, and mixtures thereof, with or without mercury. Flow of current takes place through the gas or vapors present when proper voltage is impressed on the electrodes, due to a flow of negatively charged electrons driven from one electrode and attracted or pulled to the other. Light is produced whose color is characteristic of the gas or vapor used.

Sign tube displays are usually of the cold cathode, positive column classification. The current flow is 25 milliamperes (0.025 amperes) at 15,000 volts, necessitating a transformer to step up the voltage of the ordinary lighting circuit. The low amperage, in spite of the high voltage, means relatively low power consumption. For example, on this basis the power consumed in lighting a section of tubing, which may be as much as 40 to 50 feet in length, is 375 watts. This is low for the quantity of light produced when compared with the power requirement of incandescent lamps to accomplish the same purpose.

The development of the sign tube from the original simple neon tube has broadened considerably. After the original red tubing (neon in clear glass) had been introduced and applied, variety was demanded and the first blue tubes were made. These resulted from the addition of a few drops of mercury to ordinary neon tubes. The mercury vapor was sufficient to mask the neon color entirely and imparted a distinct blue shade to the glow. This combination did not function satisfactorily in cold weather for outdoor use because the mercury vapor condensed and the blue color faded. If the weather was cold enough the tube became red. To offset this fading, mixtures of neon and argon with mercury are ordinarily used, and in extremely cold climates a little helium is also added to increase the electrical resistance of the tube and thus make it operate at a higher temperature.

Originally, green tubes were produced by using mercury in conjunction with rare gases in amber or uranium glass tubing. Tubing of this type absorbs the blue light emitted by the mercury. Since the green light emitted by the luminous mercury predominates in balance of the unabsorbed visible light, the tube appears green, even though the unscreened light is predominantly blue.

COMMERCIAL COLOR CHART

Clear or colored glass (uncoated)

Color	Gas	Pressure	Glass	Mercury
Deep red	Neon	10–18 mm.	Soft red	No
Red	Neon	10–18 mm.	Clear	No
Gold (yellow)	Helium	3– 4 mm.	Noviol (amber)	No
Light green	*Argon-neon mixture	10–20 mm.	Uranium (green)	Yes
Dark green	*Argon-neon mixture	10–20 mm.	Noviol (amber)	Yes
Light blue	*Argon-neon mixture	10–20 mm.	Clear	Yes
Dark blue	*Argon-neon mixture	10–20 mm.	Purple	Yes
White	Helium	3– 4 mm.	Clear	No

* To meet extreme winter conditions, argon-neon-helium mixture is substituted.

Fluorescent Tubes

The most recent development in gaseous tubes involves the use of a fluorescent coating on the interior wall of the tubing.

Fluorescent materials are substances which, when subjected to a radiation of a given length, emit light of a longer wave length. In this way, for example, invisible light, *i. e.*, ultra-violet light, causes a fluorescent material to emit light which is visible.

A coating of fluorescent material may be placed on the inside wall of a sign tube so as to produce light, attractive to the eye and usually of greater intensity than the light from the ordinary sign tube. The coatings selected are especially reactive to ultra-violet radiation, which is produced within the ordinary sign tube particularly when mercury is present. Whereas in the original discharge tubes of this type there was no effective means of utilizing the ultra-violet produced within the tubes, recent developments have put this radiation to work. The "extra" light produced in this way affords not only new and more attractive colors from rare gas discharge tubes, but greater efficiencies in light output.

The following table lists the fluorescent materials, known as phosphors, in use today in fluorescent coatings:

Phosphor	General Color Produced
Calcium tungstate	Blue
Magnesium tungstate	Blue-white
Zinc silicate	Green
Zinc beryllium silicate	Yellow-white
Cadmium silicate	Yellow-pink
Cadmium borate	Pink

Mixtures of the phosphors are made up to vary the color and to approach white light, obtainable in the so-called daylight tubing.

FLUORESCENT TUBE COLOR CHART

(Tubing coated with a phosphor)

Color	Gas	Pressure	Glass and Coating
Rose pink	Neon	10–18 mm.	Clear—Blue
Gold	Neon-argon mixtures + mercury	10–20 mm.	Noviol—Yellow
Yellow	Neon	10–18 mm.	Clear—Green
Green	Neon-argon mixtures + mercury	10–20 mm.	Clear—Green
Blue	Neon-argon mixtures + mercury	10–20 mm.	Clear—Blue
White	Neon-argon mixtures + mercury	10–20 mm.	Clear—White

Some of the advantages of gaseous tube signs, listed below, account for their immediate and widespread adoption.

1. Brilliant colors of high luminosity.
2. Shaped or formed to any requirements of size, shape, or description.
3. Effectiveness and advertising attraction due to light emitted by entire volume of tube—not built up by spots of light.
4. High efficiency and low operating cost due to greater conversion of electrical energy to light.
5. Long life.
6. Better adaptability to flashing due to instantaneous response to starting and stopping of current flow.

Fluorescent Tubing for Illumination

The fluorescent tube of the hot cathode, positive column type has been recently introduced for interior illumination. This development is of great promise and has been characterized as the greatest step forward in the field of lighting since the invention of the incandescent lamp by Edison. For the most part, these tubes contain argon at 3 mm. pressure plus mercury. The type of light produced is highly desirable. Even though the intrinsic brilliance is much lower than the very small source of the incandescent lamp because the light is produced by the coating on the inside of the glass tube and is spread over its entire length, it gives the fluorescent lamp a great advantage in the reduction of glare for direct lighting purposes.

These lamps thus far are essentially low-power light sources, available commercially in 15-, 20-, 30-, and 40-watt sizes. None the less, the efficiency of lamps of this type is a great advance, particularly in comparison with that of the incandescent lamp.

For example, the average efficiency of the 100-watt incandescent lamp is 15.8 lumens per watt. For purposes of comparison, the table below lists the efficiency of common fluorescent lamps in use today.

	Approximate Lumens per Watt		
Color	Length 18" (15-watt)	Length 24" (20-watt)	Length 36" (30-watt)
White	30	32	35
Daylight	30	32	35
Blue	18	19	21
Green	60	65	70
Pink	20	22	24
Gold	18	19	21
Red	3	3	3

Miscellaneous Neon Tubes

There are a number of neon tube devices rather widely used, including high-tension testers and detectors, lightning arresters, glow lamps, and other luminous tubes of varying size and description.

Neon has come into use as the current-carrying agent in safety devices, known as lightning arresters, designed to protect electrical instruments such as voltmeters, relays, rectifiers, etc., from high voltages. These devices, because of the peculiarities of neon, will allow hardly any current to pass below what is known as their breakdown voltages. In fact below this point the current flowing through the gas is almost infinitesimal. When once the breakdown voltage is reached, however, and it may be somewhat under 200 volts,

depending on the design of the device, current begins to flow. As soon as this occurs, the neon is ionized; its resistance greatly decreases with a corresponding increase in carrying capacity. As the result of the lowered resistance, very high currents can be conducted by a trace of neon, while in the case of other gases only moderate currents can pass. Unless subjected for a long period to the action of the current, these devices are able to function many times, a small tube a half inch in diameter, with gas at very low pressure, conducting as much as ten amperes for a few seconds, or several thousand amperes for a few microseconds. On overload protective devices, such a tube may operate a heavy duty circuit breaker.

Lightning arresters are also used to protect the insulation on the windings of certain types of motors from surges such as those caused by the sudden opening or closing of switches under load.

The spark plug tester is a neon tube developed as a trouble finder in automobile engine testing, the tubes glowing brightly on a properly functioning spark plug and remaining dark on a foul plug.

Another use of neon is in the high-voltage indicator (Figure 3) which consists of a highly sensitive neon discharge tube equipped with special electrodes and assembled in a glass housing equipped with brass ferrules. Its characteristics are such that it will glow

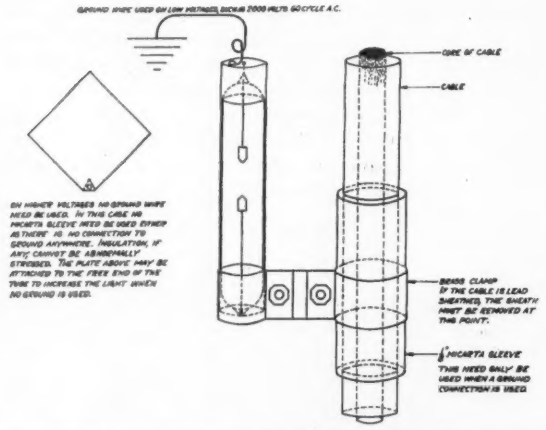

FIGURE 3.—GENERAL METHOD FOR MOUNTING HIGH-VOLTAGE INDICATORS

when subjected to comparatively low voltages with the passage of an infinitesimally small current. These act as indicators on high-tension cables to determine whether or not the cables are "alive" and find application in power and transformer stations of the various lighting and electrical power companies. This application is of interest because of its safety-first feature. The device indicates, in other words, whether an electric power transmission line is "alive" or "dead."

The neon- (or argon-) filled negative glow lamp consists of a bulb filled with rare gases with two magnesium electrodes inside the bulb and a high resistance inside the base. When the lamp is operated on direct current, the gas is ionized and light is emitted, surrounding the negative electrode with a soft pinkish glow or corona. On alternating current first one electrode and then the other is negative and each glows in turn, but at 60 cycles the alternations are so rapid that both appear to be continuously lighted. The actual amount of light emitted, about $^1/_{500}$ candle power, is small but the lamp makes an excellent indicator.

The glow lamp is also built with electrodes in the form of letters and figures for display; house numbers may be made up and similar uses developed.

Helium

The major use of helium is in lighter-than-air craft. Since helium is present in the atmosphere, it is frequently suggested that helium from that source be used for inflation of balloons. Actually the amount of helium found in air is too small for consideration for such an application. Georges Claude, in answer to a question of this sort, commented that if a commercial oxygen column of average capacity had been started in operation at the time of the birth of Christ and all the helium were collected from the air passing through that column, there would be sufficient helium to fill one zeppelin by the year 2000!

Fortunately we in the United States do not have to rely on the atmosphere for helium for this purpose, but can get it from natural gas in the western and southwestern parts of the country. Today the Federal Government controls the helium resources of this country and operates the one plant producing helium from natural gas.

Due to the fact that helium will not burn or explode and its lifting power is $^{11}/_{12}$ that of hydrogen, it is admirably suited for use in balloons. (The lifting power of a gas under room conditions of 70°F. and atmospheric pressure may be determined by a comparison of its density with that of air. For example, from Table 1 a cubic foot of air under these conditions weighs 0.07494 pound whereas a cubic foot of helium weighs 0.01034 pound. The difference, namely 0.06460 pound, is the weight which one cubic foot of helium at 70°F. and atmospheric pressure will lift.)

Within recent years helium has found application in the production of artificial atmospheres which are supplied to divers and tunnel workers. Such operations are carried on under pressure and when compressed air is used the nitrogen present will dissolve in the blood stream. Should an individual, after working under such conditions, be allowed to reach the atmosphere at normal pressure within a short period of time, the nitrogen dissolved in the blood stream will be released in the form of minute bubbles, causing the pathological condition known as the "bends."

On the other hand, if these workers are supplied with an artificial atmosphere, which may be a mixture of 80 per cent helium and 20 per cent oxygen, it is found that the period of decompression is much more rapid and the worker can safely return to normal atmospheric

conditions with considerably less hazard. The explanation of this phenomenon is to be found in the fact that helium is extremely insoluble.

The medical profession has also investigated the possible use of artificial atmospheres containing helium in the treatment of diseases where breathing is difficult. For example, in the case of asthma, a patient will secure great relief after a short period of time in an atmosphere of helium and oxygen. Since the density of such a mixture is less than the density of air, the patient can inhale a volume of the mixture large enough to give him his requirement of oxygen even though his air passages are partially blocked.

Commercially, atmospheric helium has little application, although it is used occasionally in display sign work, pure or mixed with neon or other rare gases to modify the characteristics of argon or neon.

Krypton and Xenon

Krypton and xenon find some application in the field of gaseous tube lighting since it has been found that additions of very minute quantities of these gases will bring about decided changes in the electrical characteristics of argon or neon.

Recently a tube containing krypton and xenon has been developed in connection with high-speed photography to provide a flash of light of extremely short duration. An exposure is made with the camera shutter open and the time of exposure is the duration of the flash of light. This principle makes use of a controlled electric current obtained from a large electric condenser charged almost to the point of breakdown and designed to discharge through an enclosed body of gas, thus supplying an almost instantaneous flash of high-intensity light.

One example of a tube of this type containing mercury and krypton at 6 mm. pressure is shaped into a coil, the two ends of which terminate in a common bakelite socket for mounting in a reflector. The flash speed is roughly proportional to the capacity of the condensers used; the greater the condenser capacity the longer the flash. It is claimed that, by the application of 30 microfarads, there is a flash of intense soft light of a duration estimated at approximately one fifty-thousandth of a second. As compared with an ordinary flash bulb or flash powder, which produces a flash averaging one-fortieth of a second in duration, the condenser discharge permits the taking of pictures with practically instantaneous exposures.

According to recent authoritative information, it would seem that the rarest of all the rare gases, krypton and xenon, may find a field of their own and replace argon, the most plentiful, just as argon has replaced the more abundant nitrogen. Claude has recently announced his findings with respect to their usefulness as a substitute for argon in filament lamps. He finds that a 25-watt filament lamp containing krypton and xenon will operate at an efficiency one-third greater than the same lamp containing argon.

The future will unquestionably bring forth even more important applications of these rare gases than have thus far been developed. There are at least two possibilities immediately before us: first, the application of krypton, or a mixture of krypton and xenon, in the incandescent lamp to replace argon, and secondly, the use of the fluorescent luminous tube for general illumination.

Editors Outlook

(*Continued from page 501.*)

The sudden abundance of jobs is not an unqualified blessing to the schools. Some pupils, scholastic weaklings as a rule, who look at school as preparation for a job only, have left school to go to work before graduation. This is a step which they may regret later. Others, seeing a job in sight, or even having a job before graduation, have given scant attention to their lessons, making a miserable record in the latter part of the year, to the great distress of their teachers.

On the other hand, after graduation many boys are entering large machine shops where technical work of a high order is carried out. In the curriculum of the apprentice school of these shops we find chemistry and physics—fundamental science. Significant indeed is the emphasis on fundamental principles of elementary science in shops. In fact, those pupils who have studied elementary chemistry or physics in school, preferably with self-performed laboratory experiments, have a favorable rating with employers.

The same is true of those who enter training for the various branches of military service. Unless already prepared, both privates and officers must first be grounded in their elementary mathematics and physical science as the foundation for specialized work.

Thus in the time of emergency we see in its true light the value of the fundamental training in chemistry we as teachers are trying to impart. In times like these a course called chemistry, but covering transportation, domestic economy, first aid, ecology, astronomy, music, geography, physiology, and mechanics—all combined by the egg-beater method—simply does not belong.

No more convincing argument need be offered for the sound value of a course in chemistry, unqualified.

E. C. W.

The Temperature–Composition Diagram of the Partially Miscible System Water–Isobutyl Alcohol

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THEORETICAL DISCUSSION

WHEN two pure, chemically similar, volatile liquids are mixed, no appreciable energy or volume effects are observed, regardless of the proportions of the components employed. Since the concentration of each component is decreased by addition of the other, the vapor pressure of each is correspondingly decreased. The partial vapor pressure of either component in the vapor phase, however, is exactly proportional to its mol fraction in the liquid phase, and the requirements of Raoult's law are fulfilled. Such solutions exhibit a constant environmental effect throughout the entire composition range and are accordingly classified as *ideal*.

If the two components are chemically dissimilar, deviation from ideality occurs, which becomes increasingly pronounced as the dissimilarity increases and the temperature decreases. Such deviations become manifest in vapor pressure–composition diagrams by departure from the straight-line relation of Raoult's law. With increasing dissimilarity, it is obvious that a condition should eventually be reached at which a vapor pressure–composition diagram would exhibit both a maximum and a minimum for some definite temperature. These are not actually realized, for at the given temperature two saturated phases appear, which are in equilibrium and whose compositions depend upon the condition that the partial pressure of each component must be the same from each phase. These two-component systems are, therefore, univariant, and for a given temperature the composition of each phase is constant and independent of the proportions of the components. The addition of either component results only in changing the relative volumes of the two liquid phases. The vapor pressure of such a system remains constant during distillation, and, consequently, a distillate of constant composition results as long as the two liquid phases are present. These systems, therefore, behave like constant-boiling mixtures. During distillation, the liquid phases continually decrease in volume and eventually one of them disappears; the composition of the remaining liquid phase depends upon the total composition of the original two-phase system.

It is clear, therefore, that the variation of intermolecular attractive forces, acting between different components, gives rise to varying degrees of deviation from ideality. This leads to the simple and convenient method of classifying solutions according to the type and magnitude of the deviation shown. Thus we have, (1) components completely miscible, (2) components partially miscible, and (3) components completely immiscible. Of these, the second offers the greatest number of difficulties in obtaining the necessary data for the construction of the temperature–composition diagram. This is due to the fact that the distillate samples break down into double liquid layers at the relatively low temperature (of the room) at which the compositions are determined. The purpose of this paper, therefore, is to present a relatively simple method for obtaining the necessary data for the temperature–composition diagram of partially miscible liquid systems. The authors believe that the method described will apply to all such systems with possible slight variations as the case requires. The system water–isobutyl alcohol was used in this study.

THE REFERENCE CURVE

The initial step in the procedure was to construct a reference curve by plotting the refractive indexes of prepared solutions against the corresponding known compositions. In order to obtain a smooth, continuous curve for the entire composition range, it was necessary to employ a third solvent in which both water and isobutyl alcohol are soluble. The necessity for the third solvent is obvious, since water and isobutyl alcohol are but partially miscible in each other and, therefore, form two saturated-solution layers over a rather large total composition range. It is important to obtain homogeneous systems for the whole range in order to determine the refractive indexes. The third solvent used was 95 per cent ethyl alcohol.

A series of 24 mixtures of isobutyl alcohol and water was used in the preparation of the reference curve. These were prepared by adding increasing quantities of isobutyl alcohol in increments of 0.5 ml. to successive 10-ml. volumetric flasks. Water was then added to each flask until the liquid level was at the 10-ml. mark. The last five solutions of the series were made up by the addition of 0.2-ml. increments of the alcohol. A 10-ml. graduated pipet was used and care was taken to drain the pipet slowly. A double liquid layer was observed in most of the flasks. Exactly 2.5 ml. of ethyl alcohol were then added to each flask; the contents were carefully mixed. A clear, homogeneous mixture resulted in each case. The flasks were tightly stoppered and numbered; the solutions were reserved for refractive index measurements.

An Abbé refractometer was used and the temperature was regulated to 20°C. The mol fraction of isobutyl alcohol in each mixture was calculated on the basis of a total volume of 10 ml., the effect of the alcohol

present being disregarded, since this factor is automatically canceled in the reading of the unknown mixtures which were obtained during the distillation. The isobutyl alcohol used boiled between 106.8°C. and 108.0°C. at 748.2 mm. pressure. The data are shown in Table 1. The refractive indexes n were plotted as

TABLE 1

DATA FOR REFERENCE CURVE

Flask	Composition: Isobutyl Alcohol, Ml.	Composition: Water, Ml.	Mol Fraction Isobutyl Alcohol	$n_{20°C.}$
1	0.0	10.0	0.000	1.3435
2	0.5	9.5	0.010	1.3460
3	1.0	9.0	0.021	1.3492
4	1.5	8.5	0.033	1.3520
5	2.0	8.0	0.046	1.3548
6	2.5	7.5	0.061	1.3577
7	3.0	7.0	0.077	1.3597
8	3.5	6.5	0.095	1.3626
9	4.0	6.0	0.115	1.3645
10	4.5	5.5	0.137	1.3674
11	5.0	5.0	0.163	1.3695
12	5.5	4.5	0.192	1.3715
13	6.0	4.0	0.226	1.3740
14	6.5	3.5	0.263	1.3762
15	7.0	3.0	0.312	1.3781
16	7.5	2.5	0.369	1.3800
17	8.0	2.0	0.438	1.3820
18	8.5	1.5	0.524	1.3839
19	9.0	1.0	0.636	1.3856
20	9.2	0.8	0.691	1.3863
21	9.4	0.6	0.753	1.3870
22	9.6	0.4	0.824	1.3878
23	9.8	0.2	0.905	1.3883
24	10.0	0.0	1.000	1.3888

ordinates against the mol fractions of isobutyl alcohol as abscissas. The curve thus obtained (see Figure 1) was used to determine the composition of the samples obtained from the distillation of the water–isobutyl alcohol system.

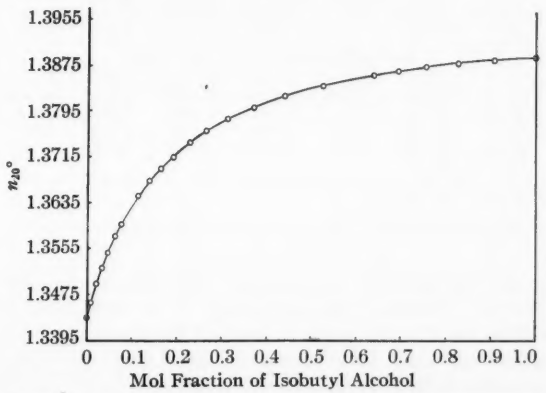

FIGURE 1.—REFERENCE REFRACTIVE INDEX–COMPOSITION CURVE

THE DISTILLATION PROCESS

Two distillations were made, one with an excess of isobutyl alcohol and the other with an excess of water. The procedure was essentially the same in both cases. The apparatus assembly is shown in Figure 2. A 500-ml. distillation flask A was used, which had a delivery tube 45 cm. long and of 5-mm. bore. The delivery tube functioned as an air condenser and was bent sharply downward (about 45°) to insure rapid passage of the distillate. The neck of the flask was wrapped with several layers of asbestos to prevent uneven heating. A thermometer with a lens front having 0.1° scale divisions was used.

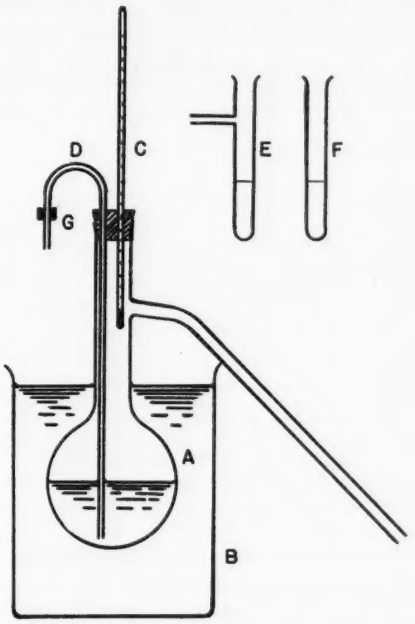

FIGURE 2.—THE DISTILLATION APPARATUS

Since it was necessary to obtain samples of distillate and residue simultaneously, arrangements had to be made to remove small quantities of the liquid from the flask without interrupting the distillation process. To accomplish this, a residue delivery tube D was made by extending a length of capillary through the stopper nearly to the bottom of the flask. The upper end was bent downward as shown in the figure. The residue receiving tube E consisted of a small length of 7-mm. tubing closed at one end and equipped with a side arm. This receiving tube was carefully graduated to one ml. The distillate receiving tube F was also graduated to one ml. A small rubber washer G, which fitted into the neck of tube E, was drawn over the end of tube D, as shown in the figure. To obtain a sample of the liquid within the flask, the delivery end of tube D was inserted into the residue receiving tube with the rubber washer effectively closing the neck. Liquid from the flask was then drawn into the receiving tube by suction through its side arm. To insure that the residue samples withdrawn from the distillation flask were representative of the mixture present, the withdrawal tube was each time blown clear of trapped liquid and the samples quickly withdrawn as described.

Instead of heating the flask directly, it was immersed in a strong solution of calcium chloride contained in a 4-liter beaker. About 250 ml. of isobutyl alcohol were

placed in the distillation flask and enough water added until, after shaking for several minutes, a definite double layer was formed. The temperature of the bath was raised slowly until the liquid in the flask just started to boil. The boiling was regulated to such a rate that the vapor front was held within 15 cm. of the outlet of the air condenser. After discarding the first few milliliters of distillate, *but while there was still a double layer present in the flask*, exactly one ml. of the distillate was collected. As nearly simultaneously as possible with the collection of the distillate sample, a one-ml. sample of the residue was collected from the alcohol layer. The temperature and barometric pressure were noted immediately.

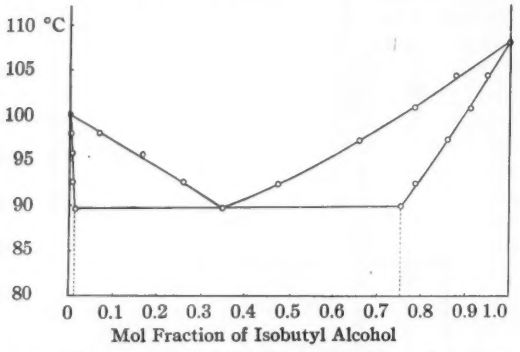

FIGURE 3.—TEMPERATURE–COMPOSITION DIAGRAM OF THE WATER–ISOBUTYL ALCOHOL SYSTEM

A double liquid layer appeared in the distillate sample after cooling. Exactly 0.25 ml. of ethyl alcohol was then added to both the distillate and the residue samples by means of a one-ml. graduated pipet. The samples were thoroughly shaken and then placed in 10-ml. test tubes. These were tightly stoppered, labeled, and reserved for the refractive index measurements. For convenience, the fractions were labeled 1*d* and 1*r*, 2*d* and 2*r*, etc., with the corresponding temperature at which they were collected.

The temperature remained constant until the double layer disappeared. After this, the temperature gradually increased. A number of samples of both the distillate and the residue were collected at temperatures varying between the boiling point of the two-phase mixture and the boiling point of the isobutyl alcohol. Great care was taken to raise the temperature very slowly after the double layer disappeared. When the boiling point of the isobutyl alcohol was approached closely, the distillation was stopped.

The distillation system was then carefully cleaned and 250 ml. of water were added to the flask. Isobutyl alcohol was now added until, after several minutes of shaking, a double layer was formed. The distillation process was repeated exactly as described above, distillation being stopped when the boiling point of pure water was closely approached. In every case, one-ml. samples of the distillate and the residue were obtained; 0.25 ml. of ethyl alcohol was added to each sample.

After the second distillation was completed, the refractive indexes of the various fractions of the distillates and the residues from both distillations were determined at the reference temperature of 20°C. By applying the refractive indexes to the reference curve, the mol fraction of isobutyl alcohol in each sample was determined. The data are assembled in Table 2. The mol fractions were plotted, as abscissas, against the temperatures (corrected to 760 mm. of mercury) at which each sample was collected, as ordinates. The boiling points and refractive indexes of the pure components were also plotted. A temperature–composition diagram of the partially miscible system water–isobutyl alcohol was thus obtained. This is shown in Figure 3.

It is to be noted that the effect of the ethyl alcohol on the refractive indexes of the mixtures is canceled in the described procedure; it functions *only as a mutual solvent to produce homogeneous solutions of the components*. Without this procedure it is impossible to determine the refractive indexes of the distillates (and, therefore, their total compositions) except for those samples whose compositions approach very closely those of the pure components. Only one or two points would be obtained for the liquid and the vapor curves at opposite ends of the temperature–composition diagram, a number certainly insufficient to construct a complete diagram.

TABLE 2

DATA FOR TEMPERATURE–COMPOSITION CURVE

Temperature Observed, °C.	*Corrected to 760 Mm.,* °C.	*Observed Pressure, Mm.*	*Refractive Index at 20°C. Distillate*	*Residue*	*Mol Fraction of Isobutyl Alcohol* Distillate*	*Residue*
Distillation with excess water						
89.6	89.65	758.9	1.3795	1.3461	0.350	0.010
92.3	92.59	753.2	1.3759	1.3445	0.265	0.005
95.3	95.59	753.2	1.3695	1.3440	0.165	0.002
97.7	98.00	753.1	1.3579	1.3435	0.065	0.000
99.7	100.00	753.1	1.3435	....	0.000	0.000
Distillation with excess isobutyl alcohol						
89.4	89.65	754.2	1.3795	1.3871	0.350	0.755
92.0	92.26	754.0	1.3829	1.3876	0.475	0.785
96.8	97.07	753.8	1.3860	1.3882	0.660	0.860
100.3	100.57	753.8	1.3875	1.3885	0.785	0.915
104.0	104.27	753.8	1.3885	1.3887	0.880	0.950
106.8 to 108.0	107.31 to 108.50	748.2	1.3888	....	1.000	...

* Interpolated from the reference refractive index–composition curve.

● University Microfilms (Ann Arbor, Michigan) is making a specialty of doctoral dissertations, reproducing the complete text on microfilm and issuing planographed abstracts for distribution. This method of "film publication" might go a long way to relieve the pressure, which is becoming greater and greater.

High-School Chemistry

Semimicro Equipment for High-School and College Chemistry

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NOTWITHSTANDING the emphasis upon small-scale or semimicro methods in commercial and more advanced college laboratories, very little use is being made of them in the high-school and college inorganic field. The authors have utilized the semimicro technic in both of these laboratories and have found it to be highly successful.

Directions for the semimicro inorganic laboratory were in the main lacking when the work was first begun. Outside of E. C. Grey's book[1] and that of E. V. Hjort[2] there was nothing in this field. Following the pattern described in these foregoing books the authors worked out and had published in lithograph form a laboratory manual for high-school chemistry.[3] Subsequently, with experience garnered from the high-school field, directions were worked out for the college, these being in the mimeograph form at the present time. In the early stages the student laboratory work was carried out in a laboratory with the ordinary equipment. With plans afoot for a new science building it was decided that the new general chemistry laboratory was to be equipped for semimicro work.

The description that follows indicates the design of desks and equipment which they have found successful. In the main the equipment is similar to that used in the regular or macro work but much reduced in size.

Equipment in Student Kit[4]

1 beaker, 50-ml.
1 flask, 50-ml.
2 test tubes, 4-inch
6 test tubes, 2-ml.
4 centrifuge tubes, 3-ml.
4 vials (to collect gases—12-ml.)
2 microscope slides
1 watch glass, 50-mm.
1 graduate cylinder, 10-ml.
1 crucible (Coors 00)
1 crucible cover
1 micro burner
1 wing top
1 wire gauze, 4-inch
1 forceps
1 pipe stem triangle
1 test tube holder
1 buret clamp
1 iron ring, 3-inch
1 spatula, micro
2 glass rods—made by student
2 dropping pipets—made by student
1 micro funnel
1 funnel brush
1 triangular file

[1] GREY, "Practical chemistry by micro methods," W. Heffer and Sons, Cambridge, England, **1925,** 124 pp.

[2] HJORT AND WOODWARD, "Laboratory directions in micro inorganic chemistry," Edwards Brothers, Inc., Ann Arbor, Mich., **1933,** 103 pp.

[3] SCHILLER AND LAWRENCE, "A laboratory manual for high-school chemistry by semimicro methods," Welch Manufacturing Co., Chicago, **1938,** 163 pp.

[4] If drawer space is lacking this equipment may be kept in a small-sized box.

Acid-Base Block

This block contains the concentrated and dilute acids and alkalies. The dilute are kept in 35-ml. Barnes dropping bottles and the more corrosive in bottles stoppered with ground glass pipets. This block is kept on a special shelf in the cabinet portion of the locker.

Each block contains concentrated and dilute solutions of the common acids and alkalies. One of these sets can generally be used by two or more students.

General Chemical Block

This block (Figure 1) contains the chemicals required for experimentation. The solutions are kept in bottles of 8-ml. capacity equipped with bakelite screw caps and small dropping pipets. The solids are kept in 2-ml. fermentation tubes. Extra holes in the block are used as "test tube racks" during the laboratory period. The block is solid, 9″ × 10″, and drilled to accommodate approximately 40 solutions and 120 solids. One block is used by two students during a laboratory period. A list is also furnished indicating the location of the various materials.

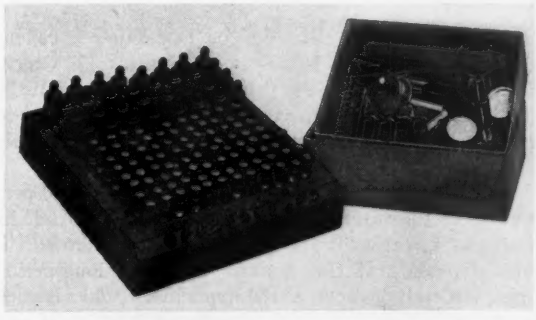

FIGURE 1.—STUDENT KIT AND REAGENT BLOCK

Special reagents are kept in Barnes dropping bottles on a side shelf. Stock solutions are kept in 8-oz. narrow-necked bottles, from which the small 8-ml. bottles in the general chemical block are filled.

General Equipment

This equipment is kept in the stock room and distributed for student use when needed:

Electrical or hand centrifuges
Hand balances with weights
Thermometers
Dry cells
Platinum wire
Blowpipe and blowpipe tips
Mohr pipets, 1-ml.
Horseshoe magnets
Charcoal blocks

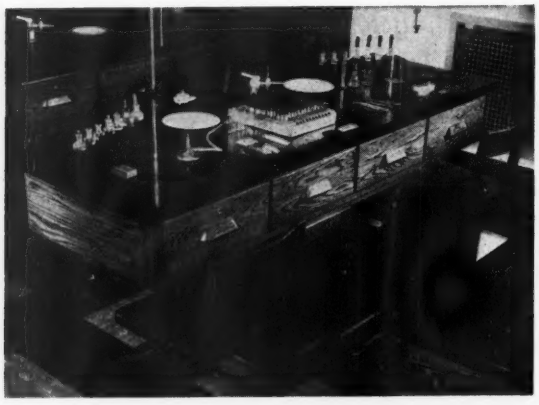

FIGURE 2.—DESK AND EQUIPMENT FOR SEMIMICRO INORGANIC CHEMISTRY

Laboratory Furniture

A special laboratory for inorganic semimicro chemistry has been designed and installed in the college. The laboratory is unique in that there are no drain pipes at the desks; in the reduced size of locker space; in the elimination of fume hoods; and in the addition of chairs permitting the student to sit comfortably during experimentation. Figure 2 shows the construction and arrangement of the desk and equipment. Each desk is equipped with two lead enameled cups, one for solid and one for liquid residue. The liquid residues are emptied into one of two sinks suitably placed in the laboratory. The laboratory, which is 20′ by 37′, accommodates fourteen tables with space for fifty-six students, or twenty-eight per laboratory period.

Advantages

The semimicro method is to be highly recommended when laboratory space and finances are limited; when it is impossible to give individual equipment; when it is desired to reduce the danger element to a minimum, to have a laboratory free from fumes, to have students seated at their work with all necessary equipment within easy reach; and in general when it is desired to have experimentation carried out with utmost economy of space, time, and materials.

Lack of experience on the part of the teacher in the use of the equipment is no drawback because most of it has a counterpart in the regular equipment; facility in its use is readily acquired. The authors will welcome comments or inquiries and will gladly extend any help possible to those desiring added information.

LETTERS

Antiseptics in Wound Treatment

To the Editor:

It is unfortunate that Ed. F. Degering's excellent summary of current trends in antiseptics [J. CHEM. EDUC., **18**, 452 (Oct., 1941)] leaves the reader with the implication that the importance of antiseptics in wound treatment is increasing while the opposite is actually true.

The amount of antiseptic required is in inverse proportion to the rate of healing of the wound. And the chance of infection is also in inverse proportion to the rate of healing of the wound. Complex long-period irrigation technics such as the hypochlorite chlorination treatment of open wounds developed by Carrel and Dakin in the last war are outmoded and being replaced by chemical agents which hasten the growth of new tissue and favor quick healing of the wound.

Latest announced development was the marketing of Epicutan by a Swedish company, Fischer of Copenhagen, just before the outbreak of the war. This protein-like substance, found in an extract of half-incubated chicks, stimulates tissue growth. This property is typical of embryonic tissues and chemists are now investigating other constituents of these tissues.

Research on growth-promoting substances in wound treatment was started in the first World War when it was discovered that maggot grubs hastened wound closing. Chemists isolated allantoin from the maggot grub secretions and identified it as a probable growth-promoting agent.

Likewise investigated and under investigation as growth-promoting agents are the sterol hormones and cod-liver oil, including the cod-liver oil vitamins, A and D, which are probably the active agents in promoting tissue growth.

The radicalness of modern procedure in wound treatment on the battlefield is shown by the technic evolved in the recent Spanish revolt. Limb wounds were aseptically excised, bound, and encased in plaster. It is suspected that the serum and pus exclusions from the wound contain growth-promoting agents. Chemists have two problems here, to neutralize the odors resulting from the decomposition of the fluid-soaked plaster, and to isolate the growth-promoting agents.

Strangely enough, the use of growth-promoting substances for wound treatment has been perfected for the higher plants.

In 1933 and 1934, Kogl, Haagen-Smit, and Erxleben isolated the growth-stimulating plant hormones, auxins

a and *b*, from urine and corn germ oil. It was later discovered that the synthetically produced lower acid derivatives of indole and naphthalene, though not chemically similar to auxins *a* and *b*, had an even greater effect on the growth of plants than the natural substances.

In addition, while stimulating the growth of cambium in the higher plants, they inhibit the growth of the lower plant forms, killing off fungi and molds. Here we have the perfect agent for wound treatment—a combination fungicide and tissue growth stimulant.

WILLIAM COPULSKY

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BROOKLYN, NEW YORK

Priorities

To the Editor:

I was very much interested in your editorial in the September issue as it describes very closely the situation we find ourselves in here. We have now been refused small amounts of several kinds of materials without which we shall find it difficult indeed to carry on efficiently with our instructional work. Foreseeing the situation early in the summer I began an active campaign on July 10. The Chemical Section of the O.P.M. on July 17 informed me:

"You can be assured that the question of how to supply the laboratories of this country with much needed chemicals is receiving careful consideration."

I was referred then to the O.P.A.C.S. and after being cut off from some materials I wrote again on August 22. In return a letter from another executive officer stated:

"The program is being considered at the moment to take care of the institutions engaged in educational or research activities."

It seems to me that if this question has been under serious consideration since the 10th of July that it is time something was coming out of it. I am hoping that it will not be necessary to resort to political pressure—although that seems to be the most fruitful approach in Washington. I hope, therefore, that you will be able to keep this matter actively before the people and count us in to help in any way possible in bringing it forcefully to the attention of the proper authorities. In my opinion it will be only a short time before rubber and cork will be under priorities and when this happens some of us will have to close up shop.

E. C. GILBERT

OREGON STATE COLLEGE
CORVALLIS, OREGON

To the Editor:

If you continue to campaign to relieve the difficulty of chemical laboratories in obtaining certain supplies and materials, we hope that you will accept our support for the campaign.

We have encountered some difficulty in having our requisitions filled and were particularly disappointed last year when we were unable to obtain a new distilled-water line for our laboratories because of the priority pertaining to any aluminum usage. We hope that a sufficient number of laboratories will also support your efforts so that there may be a campaign of sufficient strength to accomplish something.

J. W. NECKERS

SOUTHERN ILLINOIS NORMAL UNIVERSITY
CARBONDALE, ILLINOIS

Preparing Dry Ammonia

To the Editor:

I read with interest G. M. Lisk's article in the July, 1941, issue of the JOURNAL OF CHEMICAL EDUCATION concerning a "Demonstration Involving Air Pressure" in which he suggested the preparation of ammonia by "boiling concentrated ammonium hydroxide and passing the gas through Drierite." A more convenient and probably quicker method of getting dry ammonia for this experiment, and others like the ammonia fountain, is that of dropping concentrated ammonium hydroxide through a dropping funnel onto dry sticks of sodium or potassium hydroxide and collecting the ammonia by downward displacement of air. This reacts by the common ion principle and is one of the handy tricks some of us learned from our good Professor Bean, Columbia University.

WALTER Q. BUNDERMAN

JOHN HARRIS HIGH SCHOOL
HARRISBURG, PENNSYLVANIA

Concerning the Statics of the Balance Beam

To the Editor:

Your suggested note[1] on the Moyer article is acceptable to me. If we use the formula

$$T = \frac{DL}{BK + H(P + W)}$$

in which K is the pendulum leg of the beam, and H the difference of level of the knife edges, it can be seen that K is measured, not to the face of the edge, but to its center of curvature. H is affected to some extent by friction, or more probably by progressive distortion of the agate with added weight.

This distortion appears as a rounding of the edge in the observations. Added to this, the bending of the beam may cause a variation in the difference of level, so that the results are variable within small limits. The radius of curvature of the knife edge may be as much as one-fifth of the leg of the beam. For practical purposes, however, the formula can be used as it stands to show the working condition of the balance.

ARCHIBALD CRAIG

MARS, PENNSYLVANIA

[1] See page 546.

Out of the Editor's Basket

IN LAST November's issue we published a photograph and biographical sketch of Fritz Feigl, previously of Vienna. At that time there was some uncertainty of his present location. We take this opportunity to make the record complete and to let his many friends among our readers know his present location. His present address is 215 Rua Senador Vergueiro, Rio de Janeiro, Brazil. To describe his work there we quote from recent letters to an American colleague:

"... I am now here in Brazil, after having been obliged to leave my home and work in Belgium and (after) several months passed in a concentration camp in France .... I have received here from the Ministry of Agriculture the honoring charge to organize and lead a special Department of Spot Test Analysis within the mining laboratory of the Ministry. So I have an opportunity to work on my particular field with the aid of two assistants .... I am endeavoring to create here a new center for spot test analysis, as I had before in Vienna."

● A study of Per Pupil Costs in Science is being conducted by Ralph E. Keirstead, Rogers High School, Newport, Rhode Island; Joseph H. Rohloff, Aldrich High School, Warwick, Rhode Island; and Edward P. Sawin, Cranston High School, Cranston, Rhode Island. The project was undertaken in connection with the Rhode Island Educational Workshop in 1941. The purpose of the study is to determine what can be considered an adequate per pupil expenditure for instructional materials in science. Data collected show a variation between eight cents and $6.96 per pupil for instructional material in biology. Similar ranges are found in other sciences. The data available to the investigators are not extensive enough to enable them to draw significant average expenditure figures. They seek the coöperation of other science teachers in collecting data for the extension of their studies. To this end they have prepared suggested forms on which information may be recorded conveniently. They would welcome correspondence about the project.

● A new felt for hat making has just been introduced—a felt born of necessity created by the war and one that will undoubtedly become a permanent factor in the hat industry after the war is ended. Felt hats are made chiefly of foreign rabbit fur, and this has been available mainly from Continental Europe and England. The war cut off one supply source after another, leaving England as the big remaining supply.

Casein fiber, a milk by-product, rabbit fur, and a special grade of lamb's wool are the ingredients of the new felt. Of particular significance is the fact that the same processes and equipment now employed in fur-felt hat factories are used in its manufacture, and the finished product is better than all-fur felt hats in some respects. Only experienced hatters can distinguish the difference between the new and the old fur-felt.

● Archibald Craig, of Mars, Pennsylvania, has commented[1] on Moyer's "Determination of the Center of Gravity of the Beam of a Chemical Balance" [J. CHEM. EDUC., 17, 540 (1940)], to the effect that the formula used is valid only on the condition that the knife edges are all in the same plane, as would be shown by constant sensitivity at different loads. If the sensitivity (the deflection of the pointer per milligram) is less with weight on the pans than with empty pans, the level of the end edges is lower than the middle edge. A second component will then enter the equation, which will have to be solved for two unknowns. He suggests that the effect of the lowered knife edges can be eliminated if Moyer's test is made on the bare beam without stirrups or pans. (Or the sensitivity with the bare beam can also be computed, by extrapolation, from two sensitivity determinations at different balance loads and the weight of the pans and stirrups.) It might turn out, however, that the center of gravity of the beam is above the middle knife edge, so that the beam will not swing without weight on the end edges. In such a case the complete formula is necessary.

May we suggest that the change in balance sensitivity with increasing load is in part due to increasing friction at the knife edges which is not taken into account. Second, with increasing load the alignment of the balance knife edges changes. It is common to find, for example, that the balance sensitivity first increases, then decreases as the balance load is increased. Thus the end knife edges pass from a plane above the central knife to a plane below.

● The Aluminum Service Bulletin No. 1 (Aluminum Company of America, Pittsburgh, Pennsylvania) contains Selected References on Aluminum for the National Defense Industries. A lot of interesting and possibly useful information is suggested on a variety of topics: forming, machining, heat treating, welding, analysis of aluminum, as well as many of its uses.

● The Aluminum Company of America announces that notwithstanding the tremendous demands, and the enormous and rapid enlargement of their production capacity, the price per pound of ingots has been recently dropped from 17 to 15 cents per pound, with corresponding reductions in fabricated forms. (They don't say where any can actually be bought by our college purchasing agents, however!)

They go on to tell how, fifty years ago, their metal production was 9000 pounds a year at eight dollars a pound. With the new plants now under contract of construction the rate of production will be over one billion pounds per year.

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[1] See also letter on page 545.

● Steel is also on the "up and up." This industry's *annual capacity* has been increased nearly two million tons during the first part of 1941. Nearly 100 per cent of the entire capacity is being operated, it is said. And here is where some of our aluminum goes, by the way—30,000 tons of it annually, to deoxidize and purify molten steel.

● Technical problems created by the program of national defense will make the 18th Exposition of Chemical Industries, in Grand Central Palace, New York City, December 1 to 6, an event of greater importance than any in the long line preceding it.

Until now comparatively scant attention has been paid to the persistent and thorough infiltration of chemical products and chemical processes into American industrial life. Now it is being discovered that their applications are almost universal.

World War One revealed a shocking dependence, generally unsuspected up to that time, upon imported chemicals for certain industries. Developments in the present emergency are rapidly disclosing, by sharp contrast, a succession of new products that are not only independent of foreign sources, but also independent of many of the preconceived natural resources.

These are coming from the laboratory and the pilot plant, where they have been quietly nourished on the profits of private enterprise. Out of them a bewildering new economy of production is fast emerging.

This dissolving of the familiar industrial scene into a new and unfamiliar one is a repeating phenomenon, but it is being greatly accentuated and sharpened now. It has never been more vividly depicted than at the biennial expositions of the chemical industries, but this year's display holds exceptional promise because of the impact of priorities for critical materials, and the extraordinarily rapid assimilation of substitutes therefor.

● Among the News Briefs which we have seen recently is the following "flash": DEFENSE CLASS ALUMINUM QUOTA SET: Aluminum quota for U. S. defense training classes is a million pounds of sheet aluminum and 240,000 rivets each three months. Defense classes seeking aluminum must advise State Director who sends requests through U. S. Office of Education to OPM for priorities okay.

We would stack up a chemist against an aluminum riveter any day, as regards their respective contributions to national defense. So how about granting priorities for the necessary supplies to train *chemists?*

● "New Government Aids for Teachers" is the title of a 24-page publication just issued by the U. S. Office of Education, Washington, D. C. Included in the annotated listings prepared by Margaret F. Ryan, editorial assistant, are free and low-cost books, pamphlets, charts, maps, exhibits, films, slides, and other Government-prepared materials available to teachers and school officials.

● From England, where indiscriminate incendiary bombings have caused havoc to buildings with consequent injury of valuable records, comes word of a new glycerin-using method for deciphering charred documents. A process calling for chloral hydrate and glycerin is described in an article in *Nature* by W. D. Taylor and H. J. Walls, which they believe, considering the simplicity and general applicability of the process, is a distinct advance over any previous method employed.

Briefly, the method consists in treating the charred document with chloral hydrate which appears to have a clarifying action on the burned figures or letters. This is applied in the form of a 25 per cent solution of chloral hydrate in alcohol. This is repeated several times, the document being dried at 60°C. between each application, until a mass of chloral hydrate crystals forms on the surface. At this stage, a similar solution, to which 10 per cent of glycerin has been added, is applied and the document dried as before. It may then be photographed, the most suitable type of plate being a contrasty non-color sensitive one.

The method has proved equally satisfactory for typewritten and printed material. With certain modifications it has also been found to restore writing. Moreover, the reading matter is restored equally on both sides of the paper.

● A statement recently made by one of the apparatus manufacturers reads:

"The shortage of material has already limited production of scientific instruments to such an extent that many important devices, such as certain galvanometers and electrical measuring instruments, constant temperature control devices, apparatus for high-vacuum research, etc., are out of stock and Priority Certificates will be necessary before additional instruments can be manufactured."

● This year, many teachers will include consumer topics in their course material. Prices, scarcity, quality are on the minds of students and their families. Discussion of these problems is a valuable approach to almost every subject. The Consumers Union (17 Union Square, New York City) is issuing regularly mimeographed "Consumer Class Plans" to aid classroom teaching with C. U. Reports.

● One of the striking features of The Carborundum Exhibit installed recently at the Chicago Museum of Science and Industry is the reproduction of the laboratory of the late Dr. Edward Goodrich Acheson in which he created the first man-made abrasive silicon carbide to which he gave the name "Carborundum." The old laboratory, originally located at Monongahela City, Pennsylvania, is reproduced in every historic detail. There is a replica of the old work table on which was placed the iron bowl, such as used by plumbers for the melting of solder, in which Dr. Acheson created the first

few crystals of an abrasive destined to revolutionize grinding. Bending over the bowl is a life-size figure of Dr. Acheson, just as he stood when he made his momentous discovery. The crude interior of the old room has been reproduced with meticulous care and this feature of the exhibit will have a definite historic interest.

A CLEARING HOUSE FOR EXAMINATIONS

THE Committee on Examinations and Tests of the Division of Chemical Education of the American Chemical Society, as part of its present program, is trying to make available to instructors information regarding sources of chemistry examinations. In line with this policy the Committee is willing to act as a clearing house for final examinations in general chemistry. All institutions wishing to coöperate are requested to communicate with Dr. Alexander Calandra, Department of Chemistry, Brooklyn College, Brooklyn, New York, and to indicate the maximum number of final examinations that can be conveniently made available to the clearing house in February, 1942, and June, 1942. It is the present plan of the Committee to collect these examinations, to make sets, and to redistribute them. The identity of the participating colleges and high schools will not be revealed if such is their desire and their only expense will be the mailing charge.

The Committee will be happy to receive suggestions regarding this, or any other plan for the general improvement of testing in chemistry.

RECENT BOOKS

ORGANIC REAGENTS IN INORGANIC ANALYSIS. *Ibert Mellan*, Ph.G., M.Sc., F.A.I.C. The Blakiston Co., Philadelphia, 1941. xxiii + 682 pp. 15 × 23 cm. $9.00.

This is a monograph on the use of organic compounds as reagents in inorganic analysis and includes both qualitative and quantitative methods. The introductory section (24 pages) presents fundamental theories and principles; then follows a glossary of organic reagents (195 pages); and finally a section (409 pages) on methods of procedure. An appendix (11 pages) gives a classified list of the reactive groupings of most of the known organic reagents, with examples of each type.

About 225 organic reagents are described; their structure, reactive groupings, and the resulting compounds formed are shown graphically with about 580 formulas. Approximately 230 qualitative and spot tests and 240 quantitative methods (colorimetric, gravimetric, and volumetric) are presented. The sensitivity, amount determinable, accuracy, and the interfering substances (with instructions for their elimination) are given whenever possible. Many references to the original sources are listed throughout the book which greatly enhance its usefulness.

The book will be useful to every analyst and a valuable addition to any chemical library.

JOHN H. YOE

UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA

THE THEORY OF ORGANIC CHEMISTRY. AN ADVANCED COURSE. *Gerald E. K. Branch*, Ph.D., Professor of Chemistry, and *Melvin Calvin*, Ph.D., Instructor in Chemistry, University of California. Prentice-Hall, Inc., New York City, 1941. xix + 523 pp. 49 figs., 55 tables. 15 × 23 cm. $4.00.

The theory of organic chemistry is clearly too large a subject to be covered in a book of normal size. Also, although everyone will agree that some topics belong in theoretical organic chemistry, there will be disagreement on others. The authors have given in their book a discussion of "electronic structural theory, and its application to organic chemistry" with particular emphasis on resonance.

The chapters of the book are titled: I, The Development of Structural Chemistry; II, Atomic Structure; III, Molecular Structure; IV, Group Interaction; V, Physical Properties; VI, Equilibrium—Acid Strength; VII, Energy Relationships in Some Other Reactions; VIII, The Rate Factor in Chemical Behavior; IX, The Reactions of Acids and Bases with Neutral Substances—Three-Center Reactions; X, Reactions of the Double Bond.

Many concepts are explained more thoroughly than is usually done, and the book is interestingly written. Points which are thought-provoking are raised. There are many correlations in the text that are either not to be found elsewhere or are not as conveniently available. An example of the kind of correlation that should be interesting and useful to the organic chemist is the fit of acid strength of acids with a formula involving a set of inductive constants for various groups.

It will be worth while for anyone interested in theoretical organic chemistry, be he a student or a research worker in the field, to read the text. The book is made more useful by the inclusion of some fifty-five tables which present various data such as bond energies, atomic radii, acid strengths, and relative rates of reaction of chlorides with iodide ion.

The book will be difficult to read in several spots. The amount of mathematical explanation needed by different readers will, of course, vary, but on the whole it is the impression of the reviewer that the amount of wave mechanical material is too brief to give the reader much feeling for it if he doesn't already know it. Also there are a few places in the text where it is difficult to make out exactly what the authors mean.

In connection with such topics as acid strength, especially in the case of alkylsubstituted dibasic acids, the aldol condensation, the Cannizzaro reaction, and addition to the ethylenic linkage, more or less recent work in the literature might profitably have been quoted. In connection with acid catalysis, the important point is not raised that the rate-determining step in an acid-catalyzed reaction might be reaction with a base.

Whether THE THEORY OF ORGANIC CHEMISTRY. AN ADVANCED COURSE is suitable as the sole text in a theoretical organic course depends on what is to be stressed and the arrangement of the curriculum at the institution in question. For students who receive the physical background in other courses much of the material in the text may be superfluous, and reaction mechanisms might be emphasized more than the authors do. On the other hand, for a course that stresses the physical side of the subject and still gives an introduction to mechanisms, the text is very well suited.

S. WINSTEIN

UNIVERSITY OF CALIFORNIA
LOS ANGELES, CALIFORNIA

CHEMICAL SPECIES. *Jean Timmermans*, Professor of Physical Chemistry, University of Brussels, translated by *Ralph E. Oesper*, Professor of Analytical Chemistry, University of Cincinnati, from a revision of the French edition of 1928 made by the author for this purpose. Chemical Publishing Co., Inc., New York City, 1940. viii + 177 pp. 13.5 × 21.5 cm. $4.00.

This reviews the field of the measurement of properties of pure substances. It might well be read as a compulsory introduction to a course in physical chemical measurements. However, it is not in any sense a text for such a course, for it confines itself entirely to generalizations. For that reason it will probably seem to any experienced physical chemist like a book on "What Every Young Chemist Ought to Know." Nevertheless, it is well worth reading by anyone interested in the field, even though he may already know nearly everything in it, because of the pitfalls it points out here and there into which surprisingly eminent chemists have fallen.

The translator has produced a smooth and pleasing English version, only rarely slipping into such a Gallicism as "tractional resistance" instead of "tensile strength" (page 2). No typographical errors were noticed. In general the views of the author are unexceptionable. However, on page 37 he accepts Baker's claim to a 109° boiling point for intensively dried benzene without any consideration of the possibility of his having been deceived by superheating. On page 136 a probability is referred to as infinite rather than as unity; this is probably merely a solecism, as his own mathematics lead to the value unity. On page 117 the Angström unit is referred to as "one thousandth of a micron" instead of one ten-thousandth of a micron.

EWING C. SCOTT

SWEET BRIAR COLLEGE
SWEET BRIAR, VIRGINIA

A TEXTBOOK OF QUALITATIVE CHEMICAL ANALYSIS. *Arthur I. Vogel*, D.Sc. (Lond.), D.I.C., F.I.C., Head of Chemistry Department, Woolwich Polytechnic; lately Beit Scientific Research Fellow of the Imperial College. Second Edition. Longmans, Green and Co., London, New York, Toronto, 1941. xi + 486 pp. 45 figs. 14 × 22 cm. $2.75.

The book is written for the purpose of providing a textbook at moderate cost which can be employed by the student continuously throughout his study of qualitative analysis.

This second edition has been thoroughly revised and expanded in the light of recent developments in the field. The principal additions include: (1) a discussion of the colloidal state in the theory section, (2) a practical account of spectroscopic tests and flame spectra, (3) a detailed discussion of the technic of microqualitative analysis, including spot analysis, (4) the introduction of selected spot tests for each of the cations and anions, and (5) an account of the reactions of hydrogen peroxide, the zirconyl chloride method for phosphate separation, the hydriodic acid method for dealing with certain insoluble substances, and the addition of the reactions of thallic and zirconium compounds to the section on the "rarer" elements.

The analytical procedures include the analysis of the customary twenty-four cations including lithium, and forty-two anions including peroxide. In addition, there is a fairly extensive section on the "rarer" elements.

The organization is obviously different from that of the usual American textbook of qualitative analysis. For example, the section on theory deals with ionization and solubility equilibria very briefly, and devotes much more discussion and space to oxidation-reduction from the electrochemical viewpoint and to hydrolysis of salts. These latter discussions are as complete and detailed as in the average physical chemistry courses in this country, and hence would seem too difficult for presentation to a class in elementary qualitative analysis of the first- or second-year level. Sample calculations accompany the theoretical discussions. Notable in this connection, however, is the absence of problems in the text.

In general, the confusion so often resulting in present-day textbooks of qualitative analysis from attempting to present both macro and semimicro analysis simultaneously is happily avoided in this book. This is due to the fact that the procedures are presented entirely on the macroanalytical scale, with adequate instructions given in separate, well-defined sections to enable the student or analyst who is familiar with the regular technic to employ the semimicro or micro methods if desired.

The English student is evidently thrown very much upon his own resources to supply the details of the laboratory procedures, such as the exact quantities of reagents to use and the types of equipment to employ in any given operation. There may well be distinct pedagogic advantages in this system, since the student must develop his initiative and ability to adapt his methods to special conditions and problems. It is also true, however, that this method will require a closer supervision on the part of the instructor, who must either supply many of the missing details himself, or else constantly check each student's interpretation of the procedures to avoid too much lost motion. Details of the spot tests are much more complete than those of the other tests described.

Relatively few errors were noted in the text. The few errors which occurred in the first edition have been corrected.

Ample material is presented for a very comprehensive course in practical qualitative analysis. A selection of experiments for an introductory course is outlined in the appendix.

The author has accomplished in commendable manner the preparation of a useful and fairly comprehensive textbook of qualitative analysis. It would seem to be well suited for advanced work in the field. For elementary students many instructors would find the book difficult to use due to the sparsity of details in the laboratory directions.

GRANT W. SMITH

THE UNIVERSITY OF KANSAS CITY
KANSAS CITY, MISSOURI

PLASTICS IN INDUSTRY. "*Plastes.*" Chemical Publishing Co., Inc., Brooklyn, N. Y., 1941. xi + 241 pp. 47 figs. 14 × 21.7 cm. $5.00.

The authors address this book to "the industrialists of the world" with the objective of clarifying confused ideas regarding plastics and presenting the advantages and limitations of a new series of materials of construction suitable for series or mass production.

The first four chapters are of a general nature dealing with definitions, descriptions of the chief thermoplastic and thermosetting resins, specifications, and molding and fabrication technic. The next twelve chapters discuss the present and prospective applications of plastics in various fields, including engineering, chemical and electrical equipment, aircraft, motor car, synthetic glue, synthetic rubber and furniture manufacture, and the textile and building industries. A final chapter discusses the special problems of design involved in plastics manufacture.

The bulk of the book is devoted to the subjects of fabrication and applications of plastics, giving a good picture of the wide variety of present applications (from teething rings to coffins and from dentures to complete airplane fuselages) and including some interesting suggestions for new uses. Some repetition is involved in the attempt to make each chapter on the applications in a particular industry nearly complete in itself.

Very little space is devoted to the methods of preparing the plastics themselves, or to the intermediate products in their manufacture, and the information given is not entirely reliable. Thus it is stated (page 13) that methyl methacrylate is manufactured from ethylene by the intermediate formation of acrylic acid, whereas this material is actually obtained from acetone through the cyanohydrin.

The book is written in simple language, can be read easily by high-school students, and is suitable as collateral reading for courses in general science or elementary chemistry.

CHARLES B. WOOSTER

RÖHM AND HAAS COMPANY
PHILADELPHIA, PENNSYLVANIA

EXPERIMENTS IN ORGANIC CHEMISTRY. *Louis F. Fieser*, Sheldon Emery Professor of Organic Chemistry, Harvard University. Second Edition. D. C. Heath and Co., Boston, Mass., 1941. x + 488 pp. 80 figs. 14.5 × 22.2 cm. $2.80.

As in the first edition [reviewed in J. CHEM. EDUC., **12**, 398 (1935)] the manual is organized into two parts, which in the present edition can be purchased either in separate volumes or bound as a single volume. Part I presents a list of student experiments, considerably more than adequate for a year's course. "Part II constitutes a miscellany of notes on procedure and technique designed for the general guidance of advanced students." It comprises five chapters dealing successively with (1) Suggestions for Advanced Work, (2) Apparatus and Methods, (3) Solvents, Reagents, and Gases, (4) Reactions (Acylation, the Grignard Reaction, the Friedel-Crafts Reaction, Reduction, Oxidation, Catalytic Hydrogenation, and Dehydrogenation), (5) Semimicro Determination of Carbon and Hydrogen. The index occupies a little more than thirteen pages and appears to be satisfactorily complete.

The experiments which comprise Part I now number fifty-two, some of which afford a choice of alternative examples or procedures. The experiment on quinones has been modified so as to include the preparation of 2-methyl-1,4-naphthoquinone, its conversion to phthiocol, from which vitamin K_1 is prepared by condensation with phytol (experiment 46), the preparation of sulfanilamide (experiment 49), and the isolation of abietic anhydride from rosin (experiment 50). Except for these changes Part I appears to have been reprinted with little or no revision, or at least none requiring repagination of the first 228 pages. The new experiments are interesting and timely, and are not too difficult or time-consuming for optional inclusion in an elementary course. Attention may be called to the unsuitability of dimethylaniline to illustrate the behavior of tertiary amines in the Hinsberg test (page 110); under ordinary test conditions it often yields a purple dye.

Part II has been extensively revised, both as to material and organization. It now requires 183 pages (78 in the first edition) and is a concise and valuable source of information on certain apparatus, reagents, and useful procedures. Much new material is included; for example, sections on manipulation of small (semimicro) quantities of materials (pages 331–6), chromatographic adsorption (pages 336–45), glass blowing (by E. B. Hershberg; pages 345–56), the Friedel-Crafts reaction. The discussions of some topics have been greatly extended, especially those on catalytic hydrogenation, on dehydrogenation, and on the Grignard reaction. The treatment of the melting-point determination has been considerably improved (*cf.*, the review of the first edition), and now includes descriptions of the Hershberg liquid-bath apparatus and of a well-designed aluminum block for use with high-melting substances. A paragraph on the micro determination of melting point is appended.

In the discussion of diazomethane as a methylating agent a fourth method for its preparation has been added (from mesityl oxide and methylamine). The poisonous character of diazomethane warrants the inclusion of more explicit precautions than appear on page 376. A serious case of poisoning by diazomethane which evaporated from ether solutions occurred several years ago in this laboratory. [See SUNDERMAN, CONNOR, AND FIELDS, *Am. J. Med. Sci.*, **194**, 469 (1938).] The initial symptoms were considerably delayed but developed into a dangerously severe pulmonary edema requiring a protracted stay in the hospital.

The statement in the preface, "Much of the new material of Part II is based upon the experiences, observations and opinions of my collaborators in recent researches," represents an attitude which will not escape the observant reader of the book, and which is probably responsible for some unevenness in the discussions. Part II is obviously not intended to be a compendium, but to present selected information practically at first hand, and this leads naturally to a presentation marked in places by a Cantabrigian (U. S.) emphasis. In the section on nitrogen gas (p. 395) a published criticism of the keeping qualities of the Fieser Reagent for removal of oxygen [QUIGGLE, *Ind. Eng. Chem., Anal. Ed.*, **8**, 363 (1936)] is ignored. The discussion of the Clemmensen reduction (pages 420–4) gives considerable attention to the Martin procedure but neglects to mention the modification suggested by Mikeska, Smith, and Lieber [*J. Org. Chem.*, **2**, 501 (1938)]. The discussion of manometers (pages 319–20) does scant justice to the Zimmerle manometer.

The comments made should not be misinterpreted: the reviewer considers this manual a very good one. It contains experimental information for both elementary and advanced students, and many teachers can read it with profit. It is well written, well printed and bound, and the illustrations (now eighty; the first edition contained forty-two) are excellent.

E. C. WAGNER

UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PENNSYLVANIA

A PRACTICAL SURVEY OF CHEMISTRY. *W. S. Dyer*, University of Arkansas. Henry Holt and Co., New York City, 1941. vii + 480 pp. 107 figs. 14 × 21 cm. $2.80.

This book is intended for chemistry courses in general education and is based on such a course taught by the author since 1926. It is not intended for students who take chemistry as part of their professional training either as chemists or in related fields such as medicine or engineering. Yet this is not a book "about chemistry," for it deals with the fundamentals of the science, treating most of the principles usually treated in an elementary text in chemistry. It differs from the usual textbooks in that it reduces to a minimum the emphasis upon the skills and information which would be useful only to one who is to continue the study of chemistry, and correspondingly increases the emphasis upon the application of chemical principles and theories to phenomena encountered in everyday life. This shift in emphasis may be exemplified by the fact that all the chemical principles are organized around familiar materials. Thus out of twenty-seven chapters, one finds three on the atmosphere, seven on water, two on salt, and seven on organic chemistry. Conspicuous also is the scanty treatment of symbolism and balancing of equations, as well as the avoidance of nomenclature and technical terminology.

The book is written in a readable style and is mature in its approach. One regrets that there has been carelessness in a few instances in statements of fact (*e. g.*, *azote* is implied to be derived from a word meaning "lazy") and, what is somewhat more serious, in statements involving the scientific method, suggesting a naive conception of the latter. On the whole, however, the book is a step in the right direction and deserves the serious consideration of those engaged in the teaching of chemistry for general education, either as a separate course or as a part of a survey course.

T. A. ASHFORD

UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

INFRA-RED FOR EVERYONE. *H. W. Greenwood*, F.G.S., M.Inst. Met. Chemical Publishing Co., Inc., New York City, 1941. 94 pp. 12 plates. 17.9 × 24.3 cm. $5.00.

This book is an attempt to produce a simple yet reasonably full account of the story of infra-red photography and its many applications, without recourse to diagrams, graphs, or tables. The chapters include discussions of light, visible and invisible; the early history of infra-red; modern infra-red photography; infra-red sensitive materials, their variety, care, and conservation; apparatus and the dark-room; sources of infra-red; infra-red for the amateur and professional photographer; infra-red in survey work (aerial and terrestrial), in art and industry, in criminology, in biology and photomicrography, in geology and paleontology, in chemistry and physics, in astronomy, in medicine.

Graphically illustrated, this book is clear and direct in its style, and the material is interesting and well presented. It is not intended to be a reference work, but serves as an admirable introduction to the material, from which the reader can go on to more technical accounts if he so desires.

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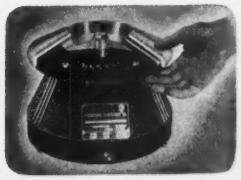

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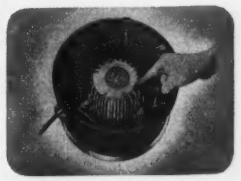

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TRADE ANNOUNCEMENTS

Adjustable Stools and Chairs

A new 8-page bulletin on Kewaunee Automatic Adjustable Stools and Chairs has just been published. The bulletin illustrates and describes these stools and chairs and also shows their use in industry and in educational and industrial laboratories.

According to the bulletin, one of the features of these stools and chairs is the patented automatic adjusting and locking device which works on the same principle as the bicycle coaster brake; when pressure is applied it locks. To increase height of stool or chair, the seat is lifted as far as desired. When upward lift is released, the seat locks instantly and securely in that position. It cannot be adjusted downward until after it has been raised above the extreme seating height where it automatically unlocks.

A copy of this bulletin can be had by writing *Kewaunee Mfg. Co., Adrian, Michigan.*

Hydrion pH Test Paper Dispenser

A new and more convenient method of using Hydrion pH Test Papers throughout the range pH 1 to 14 is provided by the plastic dispenser just announced by *R. P. Cargille, 118 Liberty Street, New York.*

Although "vest-pocket" size, this new dispenser holds and seals two 15 foot rolls of Hydrion pH Test Paper.

When using this new dispenser there is no container to open and close; the user merely pulls out and tears off the test paper needed. Color charts are visible through the transparent walls.

This outfit is claimed to be the world's simplest and handiest pH test set.

New Catalog of Rubber Testing Instruments

A new catalog of rubber testing instruments has just been published by the *American Instrument Co. of Silver Spring, Md.*

The catalog describes instruments and apparatus for making chemical and physical tests of rubber and rubber-like materials according to A.S.T.M., Federal and other standards.

The catalog is available upon application on business or professional stationery.

Booklet About pH

A ten-page booklet describing pH, what it is, the pH scale, how it is measured, how it is used in modern control, etc., has been released by the *National Technical Laboratories, South Pasadena, Calif.*, and may be obtained by teachers upon request written on school stationery. The booklet is entitled "What Every Executive Should Know about pH."

Conductivity Measurement and Control Instruments

To simplify the selection of the instrument best fitted for a given application, a condensed listing and price list of types and models has just been issued by *Industrial Instruments, Inc., 156 Culver Ave., Jersey City, N. J.*, and is available on request. The listings include the Solu-Bridge, Solu-Bridge Controller, Conductivity Bridge and Cells, Mega-Bridge, Decade Capacitor, and Distilled Water Checker. The concentration ranges or ohmages and other pertinent data are included for ready reference, together with latest prices.

Ameripol D, Synthetic Rubber

Featured by four tables, which, it is said, contain data enough to answer almost any question on the subject, the B. F. Goodrich Company has just published an eight-page catalog section on its Ameripol D synthetic rubber, used in making mechanical rubber products.

First of the tables compares the properties of Ameripol in 33 specific respects starting with "workability" and ending with "resistance to paint and ink dryers" with natural rubber and two other types of synthetic rubber, giving the rating of each in the various categories.

The second table lists the properties of typical Ameripol D vulcanized compounds, including Shore durometer hardness, percentage of elongation at break, modulus at 300 per cent elongation, ultimate tensile strength, rebound elasticity, compression set and abrasion resistance index. It also lists the results on each type of compound of 48 hours' immersion in fluids which have a solvenizing effect on natural rubber, ranging from hexane to light penetrating oil.

Table three gives the per cent volume increase after 48 hours' immersion of natural rubber and two other types of synthetic rubber, as compared to Ameripol D, while the fourth table is a rough guide to determine the service where the use of Ameripol D is practical.

Plentifully illustrated with pictures showing mechanical rubber products made with Ameripol D, the folder discusses in detail its properties, hardness, tensile strength, elongation, weight, color, odor and taste, elasticity and permanent set, tear and abrasion resistance, and resistance to flexing, oils and solvents and heat.

This catalog section 8000 may be obtained by writing *The B. F. Goodrich Company, Akron, Ohio.*

Thermocouple Data Book

A new Wheelco Thermocouple Data Book and Catalog is available from the *Wheelco Instruments Company, Harrison and Peoria Streets, Chicago, Ill.* This catalog contains pertinent data pertaining to various thermocouples frequently used by Chemists and Chemical Engineers. These data which are very detailed as to B & S Gauge, Pipe Size, Protecting Tube, and Price, are supplemented by diagrams and cross-sectional views of many different types of thermocouples.

The advice heading some of the sections about proper methods of selecting thermocouples should be particularly interesting to chemists who might be not too certain about the details.

A section in this catalog entitled "Construction of Thermocouples" gives suggestions concerning the methods of making one's own thermocouple. While this is admittedly not a complete description of the best methods, it should, nevertheless, prove itself to be very helpful.

Fisher Electrophotometer

The new AC Model Fisher Electrophotometer is described and illustrated with the aid of photographs and graphs in a leaflet obtainable upon writing to the *Fisher Scientific Company, Pittsburgh, Pa.*

In this leaflet are three graphs which are said to be representative of the types of curves which can be made from series of Electrophotometer readings of prepared standards. It is claimed that once a calibration curve has been plotted there is no need to use standards with each determination. This produces an appreciable saving in time and reagents, and reduces the possibility of errors. Once a curve is plotted, it acts as a permanent full-range standard.

It is further claimed for those solutions that follow the Lambert-Beer Law it is not necessary to refer to a curve. The logarithmic scale of the AC Model Electrophotometer is read and multiplied by a single simple factor to give results directly in the desired units.

Furnished with the Electrophotometer is the 50-page printed manual "Colorimetric Analysis with the AC Model Fisher Electrophotometer," which includes detailed instructions for operation of the instrument, many typical methods and lists of solutions and apparatus required for each method described.